UNIVERSITY OF BIRMINGHAM

PERSISTENT ORGANIC POLLUTANTS IN LACUSTRINE ENVIRONMENTS

by

Congqiao Yang

M.Sc, B.Sc (Hons)

A thesis submitted to the University of Birmingham for the degree of

DOCTOR OF PHILOSOPHY (Ph.D)

Division of Environmental Health Risk Management

College of Life and Environmental Sciences

School of Geography, Earth and Environmental Sciences

The University of Birmingham

Edgbaston, B152TT

United Kingdom

Feb 2014

UNIVERSITY OF
BIRMINGHAM

University of Birmingham Research Archive

e-theses repository

This unpublished thesis/dissertation is copyright of the author and/or third parties. The intellectual property rights of the author or third parties in respect of this work are as defined by The Copyright Designs and Patents Act 1988 or as modified by any successor legislation.

Any use made of information contained in this thesis/dissertation must be in accordance with that legislation and must be properly acknowledged. Further distribution or reproduction in any format is prohibited without the permission of the copyright holder.

Abstract

Water samples taken from nine English freshwater lakes from a mix of urban, rural, and remote locations on 13 occasions between April 2008 and February 2012 were analysed for selected non-dioxin like-polychlorinated biphenyls (PCBs), tri- through hexa-polybrominated diphenyl ethers (PBDEs), and the three main hexabromocyclododecane diastereomers (α-, β-, and γ-HBCD). Concentrations of PCBs and HBCDs declined over the sampling period with half-lives of 3.8 and 5.1 years, respectively. Concentrations of PBDEs and HBCDs varied seasonally with higher levels found in colder periods. In addition, concentrations of PCBs, HBCDs, tri- through deca-BDEs, and 32 selected "novel" brominated flame retardants (NBFRs) were measured in radiometrically-dated sediment core slices taken in summer 2011/2 from seven of the same English lakes. Temporal trends in contamination with "legacy" persistent organic pollutants (POPs) generally accord with historical trends in UK manufacture and use, with PCB contamination at all lakes increasing from ~1950, peaking generally between the late-1960s and mid-1980s, before declining steadily thereafter. Penta-BDE congeners displayed signs of decline in response to recent restrictions and bans on their use. In contrast, at most sites, BDE-209 displayed generally smooth increases following its initial emergence, and showed no obvious levelling off trend. This is consistent with the earlier introduction of use restrictions on Penta-BDE compared to Deca-BDE. Contamination with some NBFRs displayed significantly increasing trends, with concentrations of bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH) in surficial sediment exceeding the peak concentration of PCBs at one site. Spatial variation in POPs contamination of the lakes studied was evident; with regression analysis suggesting concentrations are higher in lakes with surface areas that are small relative to their catchment area, and that are closer to areas of high population density. The estimated PCB burden in the British environment is 521 tons, with TBPH (281 tons) and BDE-209 (147 tons) following not far behind. Estimated UK burdens of the remaining target compounds were significantly lower.

Acknowledgements

This work could not have been completed without the help and support of numerous people and organisations.

Greatest thanks go to my academic supervisor Prof. Stuart Harrad for his consistent help, invaluable knowledge, and scientific advice throughout the whole project. I also benefited greatly from his active collaborations with key scientists and research organisations in the field of POPs research. Additionally, as an international student studying in the UK, his encouragement and understanding in many aspects are heart warming and highly appreciated.

Sincere thanks go to Prof. Neil Rose, Simon Turner, Ben Goldsmith, and Handong Yang from University College London for their amazing assistance with English lake water and sediment core sampling and radiometric dating. Field work practice, English countryside exploration, and local English beer tasting are all wonderful memories.

Further sincere thanks go to our collaborators Sara Losada Rivas, and Jon Barber from CEFAS providing training in NBFR analysis, as well as their great assistance and invaluable advice during my several secondments in their lab.

I thank profusely also Chris Marvin and his team members Gordia MacInnis, Julia Jia, and Lina Thiessen for their amazing assistance with work on the Niagara River suspended sediments during my secondment at Environment Canada in Burlington. Special thanks to you for cherry picking and the Niagara River tour.

I acknowledge gratefully the funding of my PhD studentship by the Chinese Government and Chinese Ministry of High Education, the School of Geography, Earth and Environmental Sciences, and CEFAS.

I also acknowledge with thanks Mrs Catalina Ibarra de Moore, Dr. Mohamed Abou-Elwafa Abdel-Ghalil Abdallah, and Dr. Jennifer Desborough for providing the data reported in this thesis on POPs concentrations in water samples between April 2008 and April 2010. Their hard work is highly appreciated.

Next I thank my fellow PhD students and friends in Room 216 and 209 for all their help and company over my time at the University of Birmingham. We had so many good times together which will remain great memories forever.

Finally, immense appreciation goes to my family for their continued love, support and encouragement. A very special thanks to my extremely tolerant husband for his company and unconditional love. I will be grateful forever.

Table of Contents

List of Tables

Chapter I Introduction

Chapter II Sampling & Analytical Methodology

Chapter Ⅲ PCBs and "Legacy" BFRs in English Lake Water

Chapter Ⅳ Temporal Trends of PCBs, "Legacy" and "Novel" BFRs in Radiometrically Dated Sediment Cores from English Lakes, ~1950-2011/2

Chapter Ⅴ Temporal Trends of HBCD Concentrations in Suspended Sediments from Niagara River in Canada, 1980-2012 - A Case Study for Comparison with English Lakes

Data Tables in Appendix A

List of Figures

Chapter I Introduction

Chapter II Sampling & Analytical Methodology

Chapter III PCBs and "Legacy" BFRs in English Lake Water

Chapter Ⅳ Temporal Trends of PCBs, "Legacy" and "Novel" BFRs in Radiometrically Dated Sediment Cores from English Lakes, ~1950 - 2011/2

Chapter Ⅴ Temporal Trends of HBCD Concentrations in Suspended Sediments from Niagara River in Canada, 1980-2012 - A Case Study for Comparison with English Lakes

Figures in Appendix B

Abbreviations

a-DP	Anti-dechlorane plus
APPI	Atmospheric pressure photo ionisation
BAF	Bioaccumulation factor
BEHP	Bis(2-ethylhexyl)phthalate
BEIF	Bloomsbury Environmental Isotope Facility
BFRs	Brominated flame retardants
BSEF	Bromine Science and Environmental Forum
BTBPE	1,2-bis (2,4,6-tribromophenoxy) ethane
Cefas	Centre for Environment, Fisheries & Aquaculture Science
CHAP	Chapman's Pond
CRAZ	Crag Lough
CYP	Cytochrome P450
DBDPE	Decabromo diphenyl ethane
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DDW	Distilled water
DL-PCBs	Dioxin like-PCBs
DMSO	Dimethyl sulfoxide
DSM	Dry sediment mass
EDGB	Edgbaston Pond
EFRA	European Flame Retardant Association
EI^+	Positive electron ionisation mode
EPS	Expanded polystyrene
ESI^-	Electrospray negative ionisation mode
ESIS	European Chemical Substances Information System
FM 550	Firemaster 550
GC	Gas chromatography
GFF	Glass fibre filter
GPA	Global Programme of Action for the Protection of the Marine Environmnet from Land-based Activities
GPC	Gel permeation chromatography
HBB	Hexabromobenzene
HBCDs	Hexabromocyclododecanes
HCDBCO	Hexachlorocyclopentadienyldibromocyclooctane
HOLT	Holt Hall Lake
HPLC	High-performance liquid chromatography
K_{OW}	Octanol-water partition coefficient
LOD	Limits of detection
LOI	Loss-on-ignition at 550 ˚C
LOQ	Limits of quantification

MARM	Marton Mere
Mned BNC	Micro-nucleated binucleated cells
MRM	Multiple reaction monitoring mode
MS	Mass spectrometry
NBFRs	“Novel” brominated flame retardants
PBBB	Pentabromobenzylbromide
PBDEs	Polybrominated diphenyl ethers
PBEB	Pentabromoethylbenzene
PCA	Principal component analysis
PCBs	Polychlorinated biphenyls
PFLE	Fleet Pond
POPs	Persistent organic pollutants
PUF	Polyurethane foam
PVC	Polyvinyl chloride
RA	Risk assessment
RDS	Recovery determination standards
RfD	Oral reference doses
RRFs	Relative response factors
RSD	Relative standard deviation
S/N	Signal to noise ratio
SCOP	Stockholm Convention on Persistent Organic Pollutants
s-DP	Syn-dechlorane plus
SECURE	Self enforced control of use to reduce emissions
SHBG	Sex hormone binding globulin
SIM	Selective ion monitoring
SLT	Slapton Ley
SPM	Suspended particulate matter
SSSI	Sites of special scientific interest
THOP	Thoresby Lake
TQD	Triple quadropole mass spectrometer detector
TSH	Thyroid-stimulating hormone
TSS	Total suspended solids
UCL	University College London
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
VECAP	Voluntary Emissions Control Action Programme,
WAKE	Wake Valley Pond
WHO	World Health Organization
XPS	Extruded polystyrene

Chapter I

Introduction

1.1 Overview

1.1.1 Persistent Organic Pollutants

As defined by the UNEP (United Nations Environment Programme) Stockholm Convention, persistent organic pollutants (POPs) are chemical substances that are persistent in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. This group of priority pollutants consists of pesticides such as dichlorodiphenyltrichloroethane (DDT), industrial chemicals such as polychlorinated biphenyls (PCBs), and unintentional by-products of industrial processes such as dioxins and furans. There is evidence that the occurrence of POPs in river water and sediment is clearly associated with human activities, since the highest levels occur near urban and industrial zones and downstream of wastewater treatment plants discharge (Cristale et al., 2013). Moreover, POPs are transported across international boundaries far from their sources, even to regions where they have never been produced or used, e.g., the Arctic and the Antarctic (Goutte et al., 2013; de Wit et al., 2010; Jiao et al., 2009; Ikonomou et al., 2002, 2005). As a consequence of their long-range transportation and bio-magnification, POPs pose a threat to the environment and to human health all over the globe (European Commission). While a wide range of POPs are present in the environment, the following form the focus of this study: those already listed under the Stockholm Convention such as PCBs, Penta- and Octa-BDEs (polybrominated diphenyl ethers), and HBCDs (hexabromocyclododecanes), plus Deca-BDE - which is currently under active consideration for listing under the Stockholm Convention - and 32 so called “novel” brominated flame retardants (NBFRs).

1.1.2 Importance of Studying POPs in Lakes

70% of the earth’s surface is covered with water in the form of lakes, rivers, oceans, etc. Water and sediment act as sinks for chemical contaminants introduced to water bodies from direct discharges via anthropogenic activities (e.g. sewage outfalls), dry and wet deposition from the atmosphere, and land surface run-off. POPs can circulate within the aquatic system, partitioning between various compartments via sediment-water and water-air exchange. After entering lacustrine, riverine, estuarine and marine systems, POPs can enter and accumulate in

fish and other aquatic organisms with resultant ecological risks. Moreover, fish and seafood are important components of the human diet. Fish consumption is known to have many health benefits, but the accumulation of POPs in fish constitutes a health hazard, given the known or potential toxic effects of these POPs. Therefore, the presence and behaviour of POPs in water bodies such as lakes is an important area of study.

Sediment deposited in lakes over time represents a highly accurate and reliable historical archive of POPs input into such lacustrine systems. Monitoring POPs in lake sediment cores can: 1) enhance understanding of the temporal and spatial trends of these compounds in the environment; 2) permit assessment of differences in the environmental behaviour of different POPs; and 3) provided the sedimentation rate for a given lake is known and consistent, inventories of the mass of POPs accumulated in the lake over time can be estimated.

Individual ponds and lakes are particularly vulnerable to anthropogenic contamination of their surrounding environment. Monitoring such water bodies can provide information on the spatial distribution of POPs within a specific region, with study of rural/remote sites generating insights into the influence of factors such as population density and industry on the levels and patterns of POPs contamination.

1.2 PCBs

1.2.1 Introduction

PCBs are a group of 209 congeners with the general formula of $C_{12}H_{10-x}Cl_x$ (x=1 to 5). Due to their insulating and fire retardant properties, PCBs were used in many applications, such as dielectric fluids in capacitors and transformers, hydraulic and heat transfer fluids and additives in pesticides, paints, and copying papers (Moret et al., 2005). PCBs have been used commercially since 1930, with worldwide PCB production amounting to around 1.2-1.3 million tons (Harrad et al., 1994; Breivik et al., 2002; WHO 1992). Maximum production and usage of PCBs occurred in the late 1960s/early 1970s (Sanders et al., 1994).

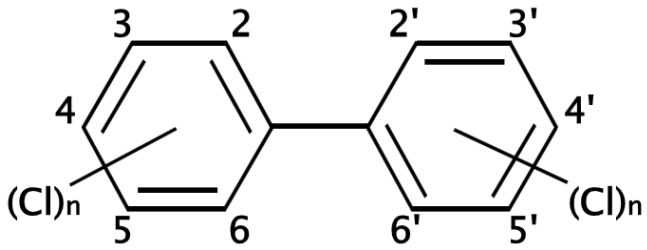


Figure 1.1 Generic structure of PCBs (n = 1 to 5)

The physicochemical properties of selected PCB congeners are shown in Table 1.1. Their low water solubility, relatively high vapour pressure and log K_{OW} values indicate their hydrophobicity, and ability to undergo long-range environmental transport and bioaccumulation. As a result of such properties combined with their historically abundant production and usage and toxicity; restrictions/bans on the manufacture and use of PCBs were introduced in most industrialised countries (including the UK) in the mid/late 1970s, culminating in 2001 with the listing of PCBs under the Stockholm Convention on Persistent Organic Pollutants (Porta et al., 2002). As a result, strong evidence exists that PCB contamination has decreased significantly since the mid-1980s in many environmental compartments including the atmosphere (Rapaport and Eisenreich, 1988; Eisenreich et al., 1989; Schuster et al., 2010) and lacustrine sediments (Gevao et al., 1997; Zennegg et al., 2007; Bogdal et al., 2008; Rose and Rippey, 2002). However, evidence also exists that they are still present at considerable levels in both indoor and outdoor environments (as summarised in Table 1.2) as a result of a combination of their extensive past use and persistence.

PCBs are considered priority contaminants, and hence monitored frequently by the USEPA (1996). Despite being banned in the late 1970s, concern about PCBs remains given the large quantities produced and used before such bans. As well as their environmental persistence, there is strong evidence that substantial quantities of PCBs remain in use in applications such as additives to building sealants (Jamshidi et al., 2007), which represents a continuing source of PCB emissions to the environment. Beside emissions from on-going use of PCBs, current sources of PCBs into the environment include: volatilisation from hazardous waste sites, landfills, sewage sludge, spills, dredge spoils and improper (or illegal) disposal of industrial wastes and consumer products, leaks from old electrical transformers containing PCBs, and incineration of PCB-containing wastes (Thomsen et al., 2007a; ATSDR, 2000). In the early 1990s, the total PCB burden in the UK outdoor environment was an estimated 400 tons, representing 1% of that sold in the UK (approx. 40,000 tonnes) (Harrad et al., 1994). This illustrates how historical production and usage of PCBs continued to exert a palpable influence on the environment long after the introduction of restrictions on their manufacture and use.

1.2.2 Environmental Fate

There is solid evidence that PCBs are easily accumulated in the environment and aquatic organisms due to their hydrophobicity and resistance to degradation (Benická et al., 1998;

Buckman et al., 2006; Streets et al., 2006; Schuster et al., 2010). It is believed that the persistence of PCB congeners generally increases with increasing chlorination (Harrad et al., 1994). Moreover, while highly chlorinated PCBs may be dehalogenated under anaerobic conditions, they are resistant to aerobic degradation (Borja et al., 2005; Bhatt et al., 2007), indicating their persistence in the environment.

The atmosphere plays an important role in the transport of POPs from sources to various environmental compartments (Bidleman, 1988; Brorstrom-Lunden, 1996). As PCBs may undergo atmospheric transport via both gas and particulate phases, they are recognised as "semi-volatile" compounds. The persistence of PCBs combined with their environmental mobility, has led to numerous reports of their occurrence in remote areas far removed from major known sources (Swackhamer et al., 1988; McVeety and Hites, 1988; Iwata et al., 1994; Muir et al., 1996; Bignert et al., 1998; Vilanova et al., 2001; Jiao et al., 2009). Moreover, the occurrence of PCBs in benthic and pelagic organisms (including krill, fish, seabird eggs, ascidians, starfishes, and urchins) off Adélie Land, Antarctica has been recently reported (Goutte et al., 2013). Table 1.2 summarises levels of PCB contamination in a number of environmental compartments including wildlife and humans.

Table 1.1 Physicochemical properties of selected PCB congeners (Li et al., 2003)

Congener	Chemical Formula	Molecular Weight	Melting Point (℃)	Water Solubility (g L^{-1})	Vapour Pressure (Pa)	Log K_{OW}	Log K_{OA}
PCB 28	$C_{12}H_7Cl_3$	257.5	58	8.85×10^{-4}	3.35×10^{-2}	5.66	7.85
PCB 52	$C_{12}H_6Cl_4$	291.9	86.5	4.78×10^{-4}	1.58×10^{-2}	5.84	8.22
PCB 101	$C_{12}H_5Cl_5$	326.4	77	1.02×10^{-4}	3.33×10^{-3}	6.38	9.14
PCB 118	$C_{12}H_5Cl_5$	326.4	110	6.83×10^{-5}	9.62×10^{-4}	6.69	9.36
PCB 153	$C_{12}H_4Cl_6$	360.9	103	3.07×10^{-5}	4.43×10^{-3}	6.87	9.44
PCB 138	$C_{12}H_4Cl_6$	360.9	79	1.87×10^{-5}	5.04×10^{-4}	7.22	9.66
PCB 180	$C_{12}H_3Cl_7$	395.3	112	1.32×10^{-5}	1.29×10^{-4}	7.16	10.4

Table 1.2 A summary of PCB concentrations in the environment, wildlife and humans (mean values in parentheses)

Matrix	Description (Sampling Year/Year Range)	Target Congeners	Concentration	Reference
Air (pg m^{-3})	Lake Thun, Switzerland (n=19)	CB 28, 52, 101, 138, 153, and 180	2-63	Bogdal et al., 2010
	Esthwaite Water, Cumbria, UK	Sum of 49 PCB congeners (CB 30-194)	51±21.5	Gevao et al., 1998
	Two sampling sites, Bursa, Turkey (2008/9)	Sum of 83 PCB congeners	37.7-1012	Salihoglu et al., 2013
Indoor air (ng m^{-3})	Offices, UK (n=33, 2003-5)	CB 28, 52, 101, 138, 153, and 180	0.82-102 (18.1)	Harrad et al., 2006
	Homes, UK (n=31, 2003-5)		0.49-9.76 (2.82)	
	Public microenvironments, UK (n=3, 2003-5)		1.08-81.5 (30.7)	
	Cars, UK (n=25, 2003-5)		0.39-6.02 (1.39)	
	Offices, homes, laboratories, Toronto, Canada (n=20, 2006)	Sum of tri- to hepta-CBs	0.8-131 (15.3)	Zhang et al., 2011a
Indoor Dust (ng g^{-1})	Homes in Amarillo/Austin, TX, USA (n=20, 2006)	CB 28, 31, 52, 101, 105, 118, 138, 153, and 180	47-620 (220)	Harrad et al., 2009
	Homes in Birmingham, UK (n=20, 2006)		5.7-860 (110)	
	Toronto, Canada (n=10, 2006)		56-820 (290)	
	Wellington, New Zealand (n=20, 2006)		11-260 (67)	
	Eastern Romania	Sum of 21 PCB congeners (CB 28-209)	10-900 (median 35)	Dirtu et al., 2012
	House dust from filters of air conditioning units or the blades of ceiling fan, Singapore (n=30)	Sum of 41 PCB congeners (CB 17-209)	n.d.-44 (9.2)	Tan et al., 2007
Soil (ng g^{-1} dw)	20 km grid intersects throughout Scotland (n=183, 2007-9)	CB 28, 52, 118, 138, 153, and 180	0.04-11.2 (1.71)	Rhind et al., 2013
	43 sampling sites, Bursa, Turkey (n=172, 2008/9)	Sum of 83 PCB congeners	1.3, 4.1, 2.2 and 1.2 in spring, summer, autumn, and winter, respectively	Salihoglu et al., 2013
	Urban and background areas, Mongolia (2010/1)	Sum of 37 PCB congeners	0.53-114 (7.4)	Mamontova et al., 2013
	E-waste dismantling site and 25 surrounding towns, southeast China (n=30, 2008)	Sum of 25 PCB congeners (CB 3-209)	0.48-90.1	Fu et al., 2011

Matrix	Description (Sampling Year/Year Range)	Target Congeners	Concentration	Reference
Water (pg L^{-1})	Esthwaite Water, a small lake in Cumbria, UK (n=6, 1996/7)	CB 28, 52, 101, 118, 153, 138, and 180	1808±468 in dissolved phase	Gevao et al., 1998
	Seine river basin, France	Sum of 21 PCBs	4300-8700	Teil et al., 2014
		CB 28, 52, 101, 118, 138, 153, and 180	2600-4800	
	Lake water (n=5) and tributary river water (n=5), Lake Thun, Switzerland	CB 28, 52, 101, 138, 153, and 180	16-80	Bogdal et al., 2010
	Kerkini Lake, the Strymon River, its main tributaries and estuary in N. Aegean Sea, Greece (2008)	CB 28, 52, 101, 138, 153, and 180	n.d.-162 ng L^{-1}	Litskas et al., 2012
	Water-column from the Seine Estuary, France (n=10, 2002-5)	A selection of PCB congeners (CB 8-209)	14.1-55.0 (26.1) ng L^{-1} (n=10)	Cailleaud et al., 2007
	Venice lagoon water (n=7, 2001)	Sum of 49 PCBs	355-1868	Moret et al., 2005
	Baltic seawater	CB 28, 31, 101, 118, 138, 149, 153, and 180	0.1-4.5 and 0.2-7.1 in dissolved and particulate phase, respectively	Bruhn and McLachlan, 2002
	Three European remote mountain lakes	CB 28, 52, 101, 118, 138, 153, and 180	26-110	Vilanova et al., 2001
	Lake Michigan water (2004)	Sum of 110 chromatographic peaks	150±11 in dissolved phase (n=7), 28±3.3 in particulate phase (n=6)	Streets et al., 2006
	Lake Huron, Superior, Erie, Michigan and Ontario		100-1600	Anderson et al., 1999
	Mississippi river, New Orleans, Louisiana, USA (2004)	Sum of 28 PCBs (CB 1 to nona-CBs)	22.2-163.4 (86.5) ng L^{-1}	Zhang et al., 2007
	Eight riverine runoff outlets of the Pearl River Delta (2005/6)	Sum of 20 PCBs	0.12-1.47 (0.77) ng L^{-1}	Guan et al., 2009
	Pearl River Estuary, China (n=36, 2005/6)	CB 4, 15, 16, 17, 18, 22, 28, 37, 56, 66, and 70	18.0-7180 in dissolved phase, 21.3-14700 in particulate phase	Chen et al., 2011
	A river affected by wastewater treatment effluent, Beijing, China (2010)	Sum of 24 PCBs (CB 1-209)	174	Yu et al., 2013
	Dianchi Lake, China (2008)	CB 28, 52, 101, 138, 153 and 180	13-72 (44) ng L^{-1}	Wan et al., 2011
	Tonghui River, China (n=16, 2002)	Sum of 12 PCBs	31.6-345 (106) ng L^{-1}	Zhang et al., 2004

Matrix	Description (Sampling Year/Year Range)	Target Congeners	Concentration	Reference
Sediment (ng g^{-1} dw)	Seine river basin, France	Sum of 21 PCBs	16-199	Teil et al., 2014
	Remote lakes, Svalbard, Norwegian Arctic (2005)	Sum of 15 PCBs (CB 18-167)	0.06-21	Jiao et al., 2009
	Coastal areas, Norwegian Arctic (2005)		0.08-0.59	
	Lake Superior (2001/2)	Sum of 19 PCBs (CB 8-206)	1.99-27.5 (3.6)	Song et al., 2004
	Lake Michigan (2002)	Sum of 39 PCBs (CB 1-206)	18.3-41.7 (26.6)	Song et al., 2005b
	Lake Huron (2002)		7.8-18.7 (11.4)	
	Lake Erie (2002)		23.0; 28.3	Song et al., 2005a
	Lake Ontario (2002)		58.3; 63.6	
	34 locations in Lake Qarun, Egypt (2011)	Sum of 29 PCBs (CB 8-209)	1.48-137.2	Barakat et al., 2013
	A river affected by wastewater treatment effluent, Beijing, China (2010)	Sum of 24 PCBs (CB 1-209)	104 and 54.7 (ng g^{-1} OC) for downstream and upstream, respectively	Yu et al., 2013
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Several fish species from the Gironde estuary, southwest of France (2004-5)	CB 28, 52, 101, 118, 138, 153 and 180	Average 150-5746	Tapie et al., 2011
	Trout, Lake Michigan (n=20, 2000-2)	Sum of 110 chromatographic peaks	Average 1600-1900 ng g^{-1} ww	Streets et al., 2006
	Trout, Lake Superior (n=23, 2000-2)		Average 290-890 ng g^{-1} ww	
	Trout, Lake Huron (n=36, 1999-2002)		Average 780-1100 ng g^{-1} ww	
	Trout, Lake Ontario (n=23, 2000-2)		Average 990-1200 ng g^{-1} ww	
	Teleost fish muscle tissues, Coastal Florida	Sum of all tri- through deca-CBs	52-41100	Johnson-Restrepo et al., 2005a
	Stingray muscle tissues, Coastal Florida		68-3160 (592)	
	Bull shark muscle tissues, Coastal Florida		2930-327000 (71200)	
	Bottlenose dolphin blubber, Coastal Florida		2510-303000 (96300)	
	Striped dolphin blubber, Coastal Florida		51700	
	Blubber samples of six delphinids species, south-eastern Brazilian coast (n=15, 2000-5)	Sum of 27 PCBs (CB 8-187)	600-257200	Lailson-Brito et al., 2012
	Mussels, estuary of the Guanabara Bay, Brazil (2006/7)	Sum of 49 PCBs (CB 8-206)	12.0-221 (ng g^{-1} dw)	da Silva et al., 2013
	Fish muscle and liver, estuary of the Guanabara Bay, Brazil (2007/8)		29.5-530 (ng g^{-1} dw)	
	Edible fish from upper, middle, and lower valleys of the Negro River, Argentina(n=29)	Sum of 24 PCBs (CB 8-209)	65-3102	Ondarza et al., 2014

Matrix	Description (Sampling Year/Year Range)	Target Congeners	Concentration	Reference
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Three tilapia fish species, lakes, pond, lagoons, Ghana (2010)	Sum of 62 PCBs	1.1-300	Asante et al., 2013
	Freshwater fish, Lake Edku fish farm, Egypt (n= 128, 2011/2)	Sum of CB 28, 52, 101, 118, 138, 153 and 180	Average 1.65-22.8 ng g^{-1} ww for individual specie	Abdallah and Morsy, 2013
	Invertebrates from a river affected by wastewater treatment effluent, Beijing, China (2010)	Sum of 24 PCB congeners (CB 1-209)	7.70-151	Yu et al., 2013
Composite apple snails (ng g^{-1} dw)	E-waste dismantling site and 25 vicinal towns, southeast China (n=40, 2008)	Sum of 25 PCB congeners (CB 3-209)	3.78-1812	Fu et al., 2011
Panda (ng g^{-1} lw)	Various tissues, China	Sum of 21 PCB congeners (CB 18-209)	24.8-854	Hu et al., 2008
Human adipose tissues (ng g^{-1} lw)	New York, USA (n=52, 2003/4)	Sum of all tri- through deca-CBs	18.9-816 (144)	Johnson-Restrepo et al., 2005b
Human blood Serum (ng g^{-1} lw)	General population from 13 locations in the UK (154 adults, 2003)	Sum of 43 PCB congeners (CB 18-203)	14-670 (median 170)	Thomas et al., 2006
	General population, Norway (2003)	Sum of CB 101, 118, 138, 153 and 180	176 for PCBs, 13.8 for PBDEs (BDE 209 included)	Thomsen et al., 2007a
	General population in urban area and surroundings of Naples (n=33), and so-called "risk area" (n=25), Southern Italy	Sum of CB 28, 52, 101, 138, 153 and 180	31.7-483 (155)	Esposito et al., 2014
	General population, aged 60-84, US (n=708, 1999-2002)	ΣPCBs(74, 118, 156, 126, 169): 8-507		Bouchard et al., 2014
		ΣPCBs(99, 138, 146, 153, 170, 180, 187): 36-1286		
	Japanese men (age 20 and > 50 group, n=20, 2010)	PCB 153: 0.10-2.14 (0.68) ng g^{-1} ww PCB 187: 0.02-0.48 (0.14) ng g^{-1} ww		Fujii et al., 2014

1.2.3 Human Exposure and Adverse Health Effects

PCBs are lipophilic, bioaccumulate in lacustrine and marine life and various animal tissues, and biomagnify within food chains (Van Oostdam et al., 2005). Given the above properties of PCBs, it is not surprising that PCBs are ubiquitous in various human samples. The primary pathway of human exposure to PCBs is via consumption of contaminated food, although indoor dust ingestion and indoor air inhalation also make appreciable contributions (Harrad et al., 2010). Fish and seafood are important dietary components especially for the residents of coastal or lakeshore areas; combined with the ability of PCBs and other POPs to biomagnify within aquatic food chains, this renders fish and seafood particularly important sources of human exposure to such chemicals.

Likely a reflection of the bans on PCB use worldwide, decreasing concentrations of PCBs have been reported in human samples. For example, PCBs in Norwegian pooled serum samples (n=21) decreased steadily from 1977 to 2003 (Thomsen et al., 2007a), and decreased modestly in archived Norwegian sera samples from 1973 to 1991 (Ward et al., 2000). PCBs in breast milk in Sweden peaked in early 1970s and showed a generally consistent downward trend thereafter (Noren et al., 2000). However, notwithstanding such welcome reductions in concentrations in human tissues; current PCB levels in human serum and milk samples are still considerable (see Table 1.2).

With respect to their adverse effects and toxicity, PCBs are a suspected factor in the substantial decline of the global eel population (Tapie et al., 2011; Robinet and Feunten, 2002) and fish eating species like otter *lutra lutra* (Sidorovich, 2000). Moreover, Nakata et al. (2002) reported the potential adverse effects caused by PCBs in organisms, e.g., immunologic changes, carcinogenicity, reproductive deficiencies, and dermatological effects (WHO 2003). PCBs are classified as probable human carcinogens (Health Effects of PCBs, USEPA, 2013). Experimental data on developmental toxicity of PCBs (Ulbrich and Stahlmann, 2004) and effects of PCBs on secondary sex ratio (Nieminen et al., 2013) have been systematically reviewed. Though many PCB congeners pose endocrine disruption and neurotoxicity, those PCB congeners sharing a similar structure and toxic mode of action with dioxin called dioxin like-PCBs (DL-PCBs, including 12 PCB congeners), are of particular concern. One such strand of evidence is a study on older US adults (Bouchard et al., 2014), which showed that PCBs, especially DL-PCBs, may have adverse cognitive effects even at serum PCB levels otherwise considered to pose low or no risk. Negative association between PCB levels in

serum and cognitive function (particularly learning and memory) has also been observed previously in a study on population aged from 50-90 in the Lake Michigan region (Schantz et al., 2001). In a study of Native Americans aged between 18 and 79 from New York State, association between higher PCB exposure and poorer executive function, memory, and motor functions were observed for individuals over 40, with serum PCB levels above a threshold of 3 μg kg^{-1} (Haase et al., 2009). Associations between higher serum PCB levels and poorer learning and memory among men, and depressive symptoms among women, were found in older residents of upper Hudson River communities, New York (Fitzgerald et al., 2008). Moreover, in animal tests, parental exposure to natural mixtures of POPs (extracted from burbot liver originating from Norwegian lakes) containing mainly PCBs, PBDEs and DDTs reduced embryo production and altered gene transcription in zebrafish embryos (Lyche et al., 2013).

Based on their toxicity, the maximum allowable concentration of PCBs in drinking water in the US is set as zero, with a *de facto* level of 0.5 μg L^{-1} due to the current water treatment technologies (USEPA 2009).

1.3 PBDEs

1.3.1 Introduction

Brominated flame retardants (BFRs) are chemicals produced for application in commercial and/or industrial materials to impart fire-resistance. BFRs act by slowing down or preventing the burning phase via reducing heat generation and production of further flammable gases. Upon exposure to high temperatures, BFRs release Br· radicals which react with the hydrocarbon molecules of flammable gases to produce HBr. The produced HBr reacts with OH· and/or H· radicals to form H_2O, H_2 and Br· radicals which can restart the cycle (van Esch, 1997). It is known that at least 75 different BFRs have been produced, with PBDEs and HBCDs representing two major classes (Alaee et al., 2003). Rapid development of newer technologies and therefore newer generations of commercial and industrial products, combined with elevated living standards and stricter fire safety regulations, has led to rapid increases in the quantities of electronic equipment and soft furnishings containing BFRs. Emissions of BFRs during the production, use and disposal of these products has led to substantial contamination of the environment and accompanying human exposure.

PBDEs consist of 209 congeners structurally similar to PCBs, with the general formula of

$C_{12}H_{10-x}Br_xO$. PBDEs are one group of the so-called "legacy" BFRs, which have been widely applied for several decades in many commercial products including plastics, rubbers, textiles, electronic components, and building materials (Hale et al., 2006; Alaee et al., 2003). PBDEs are commercially available as Penta-BDE, Octa-BDE and Deca-BDE formulations, all of which have distinct PBDE congener profiles. For example, Penta-BDE contains primarily tetra- (BDE-47), penta- (BDE-99 and -100) and hexa- (BDE-153 and -154) BDE congeners; Octa-BDE contains primarily a hepta-BDE (BDE-183) as well as hexa- (BDE-153 and -154) and octa-BDEs; while Deca-BDE contains primarily BDE-209, the fully brominated congener (La Guardia et al., 2006). The estimated total consumption in 2001 of Penta-BDEs, Octa-BDEs, and Deca-BDEs was about 7,500, 3,790, and 56,100 tons, respectively (BSEF, 2006).

The United Kingdom has consumed larger quantities of the Penta-BDE mixture than many other European countries and was the fourth largest producer of PBDEs (including Deca-BDE) in the world, with an output of ~25,000 tons annually (Alaee et al., 2003). However, though UK production and use of Penta-BDE was substantial, it was dwarfed by that of the Americas which produced 7,100 tons compared to 150 tons in Europe in 2001 (the most recent global production figures available; BSEF, 2006). North America was by some distance the principal user of Penta-BDE (95% global production), while consumption of Deca-BDE was similar in the Americas and Europe (33%, and 44% of global production respectively) (BSEF, 2006).

The abundant production and use of PBDEs in the UK has had a demonstrable impact, exemplified by reports of the presence of PBDEs in both indoor and outdoor air, indoor dust, soil, fish, harbour porpoises, human milk and blood serum, as summarised in Table 1.4. Moreover, the ubiquitous presence of lower PBDEs in UK samples in such studies indicates the continuing impact of the historical use of the Penta-BDE formulation in the UK. However, knowledge about concentrations of PBDEs in UK water bodies is scarce.

Due to concerns about their adverse environmental and human health impacts, the production and use of Penta-BDE and Octa-BDE were phased out in Europe and North America in 2004 (Hale et al., 2006), and the congeners that are the principal constituents of these formulations were subsequently listed as Persistent Organic Pollutants (POPs) under the Stockholm Convention in 2009 (SCOP, 2009). Moreover, in 2008, some applications of Deca-BDE were banned in the EU and in two US states, a complete phase-out is expected by 2013 in North America (Hess, 2010), and it is currently under active consideration for listing under the

Stockholm Convention. However, the current restriction of Deca-BDE in the EU still only includes use in electrical and electronic products (European Court of Justice, 2008), which means its use in textiles, transportation sector (e.g. automotive and aviation industries) and construction and building (e.g. wires, cables, pipes) is not restricted. Evidence of the extent of this continuing use of Deca-BDE comes from the European Flame Retardant Association (EFRA) who reported annual production to be about 5,000-10,000 tons between 2008 and 2013 (the Voluntary Emissions Control Action Programme, VECAP, 2012).

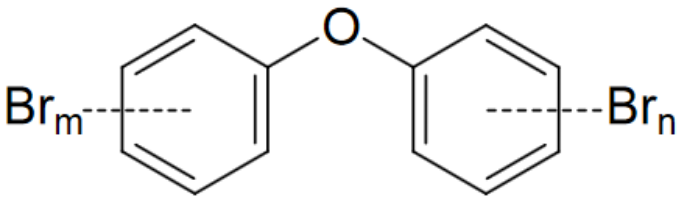


Figure 1.2 Generic structure of PBDEs (m and n= 1 to 5)

Table 1.3 Physicochemical properties of selected PBDE congeners

Congener	Chemical Formula	Molecular Weight	Melting Point (°C)[a]	Water Solubility (g L^{-1}, at 25 °C)[a]	Vapour Pressure (Pa, at 25 °C)[a]	Log K_{OW} [a]
BDE-28	$C_{12}H_7Br_3O$	406.9	64-64.5	0.7×10^{-4}	2.19×10^{-3}	5.94
BDE-47	$C_{12}H_6Br_4O$	485.8	83.5-84.5	1.5×10^{-5}	1.86×10^{-4}	6.81
BDE-66	$C_{12}H_6Br_4O$	485.8	104-108	1.8×10^{-5}	1.22×10^{-4}	6.73
BDE-100	$C_{12}H_5Br_5O$	564.7	100-101	0.4×10^{-4}	2.86×10^{-5}	7.24
BDE-99	$C_{12}H_5Br_5O$	564.7	90.5-94.5	9.4×10^{-6}	1.76×10^{-5}	7.32
BDE-85	$C_{12}H_5Br_5O$	564.7	119-121	0.6×10^{-5}	9.86×10^{-6}	7.37
BDE-154	$C_{12}H_4Br_6O$	643.6	131-132.5	8.7×10^{-7}	3.80×10^{-6}	7.82
BDE-153	$C_{12}H_4Br_6O$	643.6	160-163	8.7×10^{-7}	2.09×10^{-6}	7.90
BDE-183	$C_{12}H_2Br_8O$	722.5	171-173	1.5×10^{-6}	4.68×10^{-7}	8.27
BDE-209	$C_{12}Br_{10}O$	959.2	300-310 [b]	$< 1 \times 10^{-10}$ mol L^{-1} [b]	9.02×10^{-13}	9.97
					4.63×10^{-6} (at 21 °C) [b]	6.27 [b]

[a] Experimental data from: Tittlemier et al., 2002

[b] EU Risk Assessment Report 2002

1.3.2 Environmental Fate

PBDEs are used in an additive fashion by mixing directly with products rather than in reactive mode (where the BFR is covalently bound to the polymer matrix), which enhances the capacity of PBDEs to migrate/diffuse from treated products into the environment. The structural similarity between PBDEs and PCBs means they possess similar physicochemical

properties and display similar environmental behaviour (Borghesi et al., 2009). PBDEs are known to enter the environment via direct and indirect urban domestic/industrial sewage discharges and atmospheric deposition (Song et al., 2004), and Figure 1.3 illustrates the pathways via which PBDEs reach the environment and accumulate in humans. For example, in Australia, nationwide investigation of sediment from various water bodies, showed elevated PBDE levels at sites downstream of sewage treatment plant outfalls and in areas dominated by industrial and urban land-use types, suggesting that urban and industrial activities act as the key source of PBDEs to the aquatic environment (Toms et al., 2008). Moreover, their capacity for long-range environmental transport is evidenced by their ubiquity in the Arctic environment, which is believed to occur via long-range atmospheric and pelagic transport from source regions such as western Europe and eastern North America (de Wit et al., 2010). This is supported by the detection of PBDEs in benthic and pelagic organisms off Adélie Land, Antarctica (Goutte et al., 2013). Indeed, PBDEs have been found in almost all environmental compartments, as summarised in Table 1.4.

Regarding their environmental persistence, BDE-28 was found to undergo degradation in sewage sludge under aerobic conditions, with average (range) half-lives of 210 (130-600) and 260 (170-600) days in activated and digested sludge respectively. In contrast, BDE-28 did not undergo degradation under anaerobic conditions (half-life > 9 years; Nyholm et al., 2010). Likewise, in sewage sludge under anaerobic conditions, BDE-209 displayed a half-life of approximately 2 years (Gerecke et al., 2006). However, contrasting observations exist; for example BDE-209 did not undergo significant degradation over a 160 day duration in both activated and digested sludge under aerobic conditions and activated sludge under anaerobic conditions (Nyholm et al., 2010).

With respect to their temporal trends worldwide, for the tri- through hexa-BDE congeners that comprise the Penta-BDE formulation, BDE-183 as the principal component of the Octa-BDE formulation, and BDE-209 as the presumed marker of Deca-BDE commercial formulae, the first signs of their appearance in various sediments were generally observed between the mid-1960s to around 1970, with levels now decreasing or levelling off. Such evidence comprises sediment cores from the western Wadden Sea (Netherlands) and Lake Woserin (Germany) (Zegers et al., 2003), from Lake Greifensee, a small urban lake in Switzerland (Kohler et al., 2008), and the Great Lakes (Song et al., 2005a). There is also evidence of continuing increases in concentrations in studies of Lake Thun, Switzerland (Bogdal et al.,

2008), Lake Michigan, and Lake Huron (Song et al., 2005b). With respect to trends in other aquatic matrices, Σtri-hexa-BDEs concentrations in porpoises from UK coastal waters increased between 1992 and 1998 (Law et al., 2010). However, no sign of decreasing concentrations of banned BDE congeners was observed in snow melt from the Devon Ice Cap in Nunavut (Canada) over the period 1993/4-2007/8 (Meyer et al., 2012), reflecting the potential delayed response of some environmental compartments to recent control measures, coupled with continuing emissions from the remaining reservoir of PBDEs both in use and entering the waste stream.

BDE-209 is generally shown to have first occurred in sediment cores in the 1960s and 1970s, with levels increasing thereafter. While concentrations of BDE-209 increased rapidly following first emergence in the mid-1960s in Lake Greifensee in Switzerland and peaked in surface sediment (Kohler et al., 2008); BDE-209 concentrations were reported to be decreasing in the top layers (representing 1995/7/9) of three sediment cores from the western Wadden Sea (Netherlands), Lake Woserin (freshwater, Germany), and Drammenfjord (Norway) (Zegers et al., 2003), and in two out of three sediment cores from the Pearl River estuary in China (Chen et al., 2007). In Lake Michigan (n=3) and Lake Huron (n=3), input fluxes of BDE-209 increased rapidly following its first emergence in the 1960s-1970s in most sediment cores, and peaked in surficial sediments in four of six cores (Song et al., 2005b). Similar observations were made for PBDE trends in Lake Superior in an earlier study (Song et al., 2004). This is complemented by a recent report that BDE-209 concentrations in North American outdoor air reached a steady state at most study sites between 2005 and 2011 (Ma et al., 2013). However, this more rapid response of the atmosphere to reduced use of Deca-BDE, is likely attributable to the more rapid mixing time of this compartment.

While the vast majority of evidence of the temporal trends of PBDEs in the aquatic environment comes from outside the UK, variable trends in concentrations of BDE-209 and Σ_{16}penta-nona-BDEs were observed in six sediment cores collected in 2002/3 from the inner Clyde Estuary (Vane et al., 2010). Clearly therefore, as elsewhere, clarification is required about the response of UK water bodies to trends in PBDE manufacture and use.

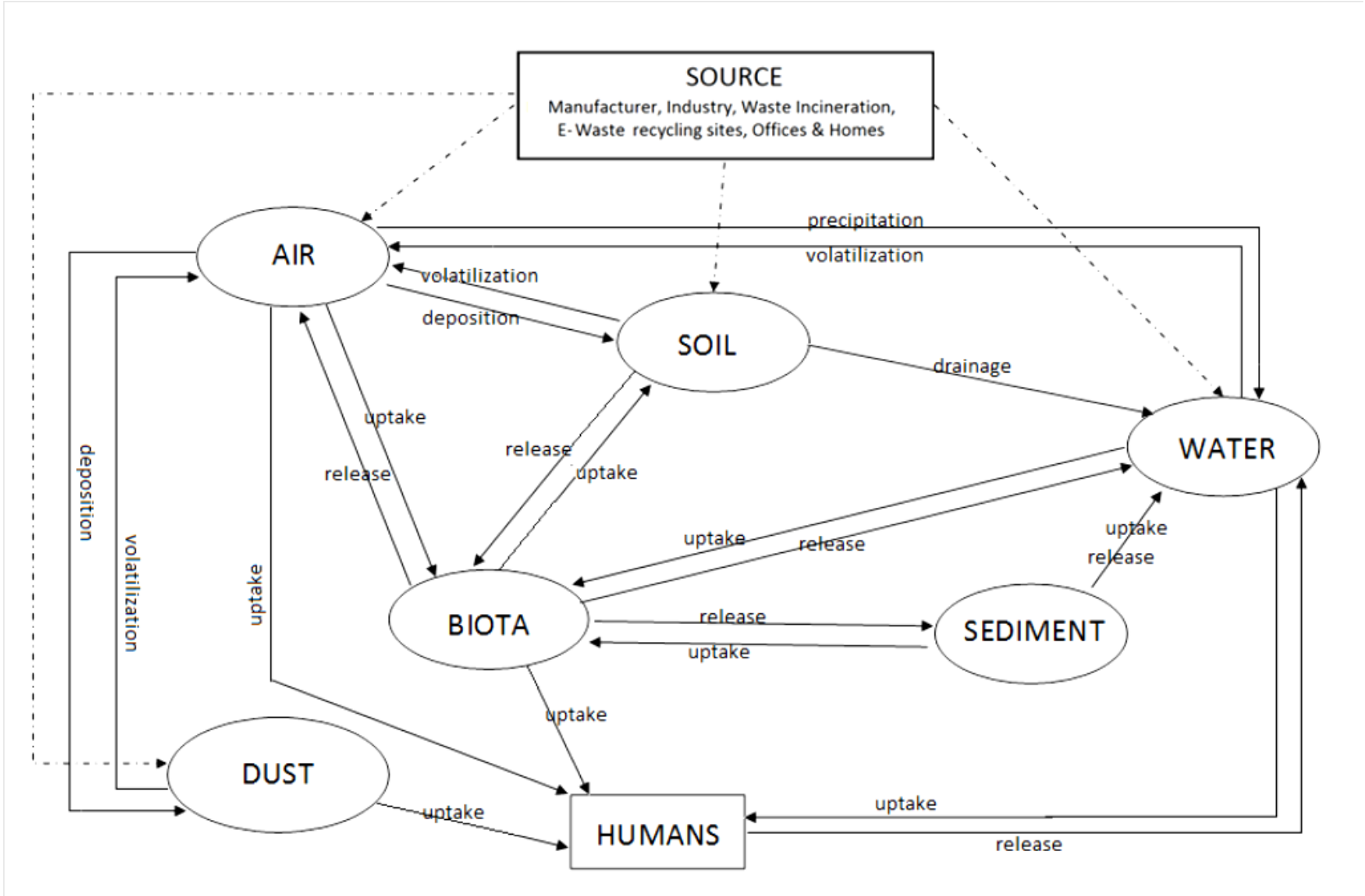


Figure 1.3 A schematic diagram showing the movement/transfer of PBDEs between various environmental compartments leading to human exposure - modified from UNEP (1999) by Drage (2013)

Table 1.4 A summary of PBDE concentrations in the environment, wildlife and humans (mean values in parentheses)

Matrix	Description	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
Air (pg m^{-3})	Rural-urban transect across a major UK conurbation	Average 2.8-23.3		Harrad and Hunter, 2006
	East-Central US	Up to 980		Hoh and Hites, 2005
	Various sites, US	ΣBDEs: 13-85; BDE-209: 0.2-65		Hoh et al., 2005
	E-waste storage facilities, Thailand	8-150		Muenhor et al., 2010
	E-waste site, China	2858-19815 (median 7149)		Yuan et al., 2008
	50 km away from e-waste site, China	80-209 (median 150)		
	Pearl River Delta, Southern China	42.0-188	196-9261	Shi et al., 2009
Indoor air (pg m^{-3})	Offices, UK	10-1416 (166)		Harrad et al., 2006
	Homes, UK	4-245 (52)		
	Public microenvironments, UK	29-162 (112)		
	Cars, UK	11-8184 (709)		
	E-waste recycling plant, Sweden		12-200	Sjödin et al., 2001
	Various working environments, Sweden		< 40 – 320	
	E-waste storage facilities, Thailand	46-350		Muenhor et al., 2010
	Dismantlers, electronic recycling facility, Sweden	ΣBDEs: 6.9-170 (60); BDE-209: 3.5-61 (25)		Pettersson-Julander et al., 2004
	Other workers, electronic recycling facility, Sweden	ΣBDEs: 9.2-43 (20); BDE-209: 3.4-13 (6.6)		
	Unexposed, electronic recycling facility, Sweden	ΣBDEs:4.4-4.8 (4.6); BDE-209: 1.3-2.2 (1.6)		
Indoor dust (ng g^{-1})	Homes, UK	7.1-250 (77)	n.d.-2200000 (260000)	Harrad et al., 2008a
	Offices, UK	16-1100 (250)	620-280000 (30000)	
	Cars, UK	54-22000 (2300)	12000-2600000 (410000)	
	Home vacuum bags, greater Boston, US (2002-7)	980-44550 (4740)		Stapleton et al., 2009
	Vacuum bag, US (2002/3)	Average 1391, 38, 2287 for penta-, octa-, deca-BDEs		Johnson et al., 2013
	Various Thai e-waste facilities	BDE-47: 7-1800 (410); BDE-99: 10-4600 (880)	250-251300 (33720) median 17800	Ali et al., 2011b
	E-waste storage facilities, Thailand	36-12000 (2200)	250-250000 (33000)	Muenhor et al., 2010
		320-290000 (43000)		
	Eastern Romania	Median 8	Median 275	Dirtu et al., 2012
Soil (ng g^{-1} dw)	20 km grid intersects, Scotland	0.09-15.4 (1.16)		Rhind et al., 2013
	From the perimeter surrounding the chicken run, Belgian (2006/7)	Maximum 5.58	<0.2-19.4	Covaci et al., 2009
	Pearl River Delta, Southern China	0.45-1.01	39.8-95.2	Shi et al., 2009
	E-waste dismantling site and 25 vicinal towns, southeast China (2008)	0.06-31.2		Fu et al., 2011

Matrix	Description	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
Water (pg L^{-1})	Seine river basin, France	80-350	420-3000	Teil et al., 2014
	Scheldt Estuary and North Sea along the Dutch coast	around 1.6		Booij et al., 2002
	Lake Thun, Switzerland	17-78		Bogdal et al., 2010
	Lake Michigan	18 in dissolved phase; 3.1 in particulate phase		Streets et al., 2006
	San Francisco Bay	BDE-47: 15.5 to 337 (54.9)		Oram et al., 2008
	Lake Winnipeg, Canada	Average 29.5		Law et al., 2006
	An urban estuary, Narragansett	BDE-47, -99, and -153: < 3		Sacks and Lohmann, 2012
	Zhujiang River estuary, China	26.1-157		Luo et al., 2008
	Pearl River Estuary, China	7.0-127 in dissolved phase; 6.2-77.6 in particulate phase		Chen et al., 2011
	Reservoir, e-waste recycling area, China	Average 21800		Wu et al., 2008
Sediment (ng g^{-1} dw)	Lake Greifensee, Sweden (2003)	1.6	7.2	Kohler et al., 2008
	Belgian North Sea and the western Scheldt Estuary	<0.2	1.1-24	Voorspoels et al., 2004
	Western Scheldt Estuary	<0.2 -18	1.5-1200	
	Freshwater tributaries of River Scheldt	<0.2-19	<0.1-320	
	Up-and downstream of a heavily industrialized town, Cinca River, Spain	2.4-41.7		Eljarrat et al., 2004
	Llobregat and Anoia River, Spain (2005-6)	22-136		Guerra et al., 2010
	River Arga, Nalón, and Besós, Spain (2012)	<0.29-812		Cristale et al., 2013
	Seine river basin, France	0.18-10.8	n.d.-297	Teil et al., 2014
	Remote lakes, Svalbard, Norwegian Arctic (2005)	0.024-0.97		Jiao et al., 2009
	Coastal areas, Norwegian Arctic (2005)	0.043-0.19		
	13 estuarine sites, Auckland, New Zealand	0.55-573		Stewart et al., 2014
	San Francisco Bay	2.1-8.0		Klosterhaus et al., 2012
	Lake Superior	0.5-3.1 (1.4)		Song et al., 2004
	Lake Michigan	1.67-3.97 (2.99)		Song et al., 2005b
	Lake Huron	1.02-1.87		
	Nation-wide various sites, Austria	n.d.-60.9		Toms et al., 2008
	Durban Bay and 13 rivers, South Africa (2011)	n.d.-7430 (423) ng g^{-1} TOC	n.d.-44500 (3208) ng g^{-1} TOC	La Guardia et al., 2013
	Five mangrove swamps, Hong Kong	0.57-14.4	1.53-75.9	Zhu et al., 2014
	12 Chinese Lakes	0.02-0.29 (0.18)	0.11-40.1 (8.2)	Wu et al., 2012
	Pearl River Delta, Southern China	2.60-60.4	32.7-2015	Shi et al., 2009

Matrix	Description	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
Sewage Sludge (ng g^{-1} dw)	Wastewater treatment plants, Catalonia, Spain (2009)	20.7-2326 (527)		Gorga et al., 2013
	Pearl River Delta, Southern China	10.8-66.8	1277-64599	Shi et al., 2009
Birds (ng g^{-1} lw)	Muscle, liver, kidney E-waste processing area, Southern China	3.44-12.5	19.4-7483	Shi et al., 2009
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Wild fish from four English rivers (2007-11)	2-44 ng g^{-1} ww		Jürgens et al., 2013
	Blubber of harbour porpoises, UK (2008)	54.6-498 (ng g^{-1} ww)	n.d.	Law et al., 2013
	Several fish species from the Gironde estuary, France (2004-5)	Average 24-237		Tapie et al., 2011
	Fish muscle tissue & liver, up-and downstream of a heavily industrialised town, Cinca River, Spain	0.2-298 (ng g^{-1} ww)		Eljarrat et al., 2004
	Trout, Lake Michigan	Average 120-350 (ng g^{-1} ww)		Streets et al., 2006
	Trout, Lake Superior	Average 39-180 (ng g^{-1} ww)		
	Trout, Lake Huron	Average 50-94 (ng g^{-1} ww)		
	Trout, Lake Ontario	Average 64-230 (ng g^{-1} ww)		
	Fish, San Francisco Bay	470-3930		Klosterhaus et al., 2012
	Seal blubber San Francisco Bay	530-5075 (adults)		
		70-1370 (pups)		
	Fish muscle tissues, Coastal Florida (2004)	1.8-306		Johnson-Restrepo et al., 2005a
	Stingray muscle tissues, Coastal Florida (2004)	2.3-83.1 (41.5)		
	Bull shark muscle tissues, Coastal Florida (2002-4)	12.4-4190 (1630)		
	Bottlenose dolphin blubber, Coastal Florida (2001-4)	30.4-4500 (1130)		
	Dolphin blubber, Coastal Florida (2002-4)	660		
	Edible fish from upper, middle, and lower from valleys of the Negro River, Argentina	22-870		Ondarza et al., 2014
	Mussels, estuary of the Guanabara Bay, Brazil (2006/7)	n.d.-3.07 ng g^{-1} dw		da Silva et al., 2013
	Fish muscle and liver, estuary of the Guanabara Bay, Brazil (2007/8)	1.92-19.4 ng g^{-1} dw		
	Three tilapia fish species, lakes, pond, lagoons, Ghana (2010)	<0.01-52		Asante et al., 2013
	Caro muscle and liver, E-waste processing area, China	42.8-211	9.57-212	Shi et al., 2009
	Cetacean samples, Hong Kong, China (2002-8)	103-51100		Lam et al., 2009
Panda (ng g^{-1} lw)	Various tissues, China	16.4-2158		Hu et al., 2008

Matrix	Description	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
Composite apple snails (ng g^{-1} dw)	E-waste dismantling site and 25 vicinal towns, southeast China (n=40, 2008)	Σ_{13}BDEs (BDE17-190): 0.09-27.7	n.d.-45040	Fu et al., 2011
Eggs (ng g^{-1} lw)	Belgian home-produced eggs(2006/7)	n.d.-3.99	n.d.-31.0	Covaci et al., 2009
Chicken faeces (ng g^{-1} dw)	Belgian (2006/7)	<0.02-22.9	<0.2-8.38	Covaci et al., 2009
Human adipose tissue (ng g^{-1} lw)	New York, USA (n=52, 2003/4)	17-9630 (399)		Johnson-Restrepo et al., 2005b
Human milk (ng g^{-1} lw)	General population, Birmingham, UK (n=35, 2010)	Σtri-hexa-BDEs 0.2-26.1 (5.95)	<0.06-0.92 (0.31)	Abdallah and Harrad, 2014
	Swedish mothers (pmol g^{-1} lw, pool sample, 2004)	BDE47:1.9; BDE 99: 0.46		Fängström, et al., 2008
	Primipara and multipara mothers, Philippines (2008)	0.61-11 (3.3)		Malarvannan et al., 2013
	Production area, China		12.3-115 (31.3)	Jin et al., 2009
	Urban/suburban Beijing, China (n=103, 2011)	0.12-8.69 (1.04)	n.d.-131 (9.85)	Shi et al., 2013
Human blood serum (ng g^{-1} lw)	General population from 13 locations in the UK	0.63-420 (median 5.6)		Thomas et al., 2006
	Electronics Dismantlers, Sweden (n=19)	median 26; 15-75 (median 37) pmol g^{-1} lw		Sjödin et al., 1999
	Computer Clerks, Sweden (n=20)	median 4.1; 3.9-17 (median 7.1) pmol g^{-1} lw		
	Hospital Cleaners, Sweden (n=20)	median 3.3; 3.1-39 (median 5.4) pmol g^{-1} lw		
	Madrid population, Spain	Median 12		Gomara et al., 2007
	New Zealand	Mean 7.17 (4 congeners)		Harrad and Porter, 2007
	Japanese mothers	Median 2.89 (13 congeners)		Inoue et al., 2006
	E-waste dismantler, Guangdong, China		n.d.-3436 (median 83.5)	Qu et al., 2007
	Residents, Guangdong, China		n.d.-377 (median 18.5)	
	Referents, Guangdong, China		n.d.-63.2 (median 5.7)	
	E-waste workers, China	77-8452 (median 382)		Yuan et al., 2008
	Referents, 50 km away from e-waste site, China	18-436 (median 158)		
	Production area, China		106-1640	Jin et al., 2009

1.3.3 Human Exposure and Adverse Health Effects

The major exposure pathways of the general public to PBDEs are now recognised as comprising: indoor dust ingestion (especially for young children and toddlers; Jones-Otazo et al., 2005; Harrad et al., 2008a; Wu et al., 2007; Abdallah and Harrad, 2014) and the consumption of contaminated food (Watanabe et al., 2003; Wu et al., 2007; Abdallah and Harrad, 2014), including breast milk (Abdallah and Harrad, 2014). Evidence of the role of such exposure pathways includes: the positive correlation observed between PBDEs in dust and paired blood plasma samples (Karlsson et al., 2007); the statistically significant positive correlations between PBDE concentrations in breast milk and in both house dust and reported dietary habits, particularly the consumption of dairy products and meat (Wu et al., 2007); and the good agreement between measured PBDE body burdens and those predicted by a pharmacokinetic model to arise from exposure via dust, diet and air (Abdallah and Harrad, 2014). Moreover, concentrations of PBDEs (BDE-28, 47, 99, 100, 153, 154 and 183) in blood serum of consumers of fish from Lake Mjosa, Norway, where very high PBDE levels in fish have been reported; were significantly higher than those of a reference group of Norwegians eating only food with background levels of contamination (Thomsen et al., 2008). Regarding occupational exposure, inhalation of highly contaminated workplace air can be a significant exposure pathway. For example, significantly higher concentrations of PBDEs were detected in the blood serum of workers at an e-waste recycling site compared to those detected in individuals from a control site 50 km distant. Similar disparities in concentrations of PBDEs in air from the two locations were also observed (Yuan et al., 2008). Likewise, significantly higher atmospheric concentrations of a range of 22 PBDE congeners (BDE-17 to BDE-209) were detected in the dismantling hall of an electronics recycling plant compared to that present outside the hall (Pettersson-Julander et al., 2004).

Besides the above pathways of exposure, dermal absorption of PBDEs via contact with dust and/or consumer goods has also been highlighted (Frederiksen et al., 2009), although its contribution to human exposure remains unclear (EU Risk Assessment Report, 2002; KEMI, 2007). Other studies have investigated pathways of human exposure to PBDEs. Jin et al. (2009) reported a lack of significant correlation between PBDEs in human milk samples and the occupation and eating habits of donors from a local area close to a chemical industrial park in China, where BFRs are manufactured; thereby indicating the existence of exposure pathways in addition to food intake and occupation. Regarding the human population

distribution of PBDEs with age, obvious correlations between PBDE concentrations in blood and donor age are not apparent (Covaci et al., 2002; Harrad and Porter, 2007; Jin et al., 2009; Thomsen et al., 2002; Darnerud et al., 1998), implying human contamination with PBDEs is not simply determined by the length of accumulation-time. However, there is fairly extensive evidence revealed by blood serum studies that toddlers/young children are more contaminated with PBDEs than adults (Thomsen et al., 2002; Thomsen et al., 2007a; Toms et al., 2009).

Evidence exists of gender-specific variation in human contamination with PBDEs. While higher average PBDE serum concentrations were found in males than females in Wellington, New Zealand (Harrad and Porter, 2007), in contrast, serum concentrations of PBDEs in females have consistently exceeded those in males in a source area, China (Jin et al., 2009). Such gender-related differences may indicate different exposure pathways to PBDEs for males and females, as well as differences in metabolism and excretion (e.g. breast-feeding). The occurrence of PBDEs in human serum, particularly in women given the concomitant implications for foetal and neonatal exposure, poses a potential public health threat.

The presence of PBDEs in biological samples, including fish, mammals, birds and humans has been reported, with alarmingly high concentrations found in the blood serum of occupationally exposed workers, as summarised in Table 1.4. Moreover, exponentially increasing temporal trends were observed in Norwegian serum samples from 1977 to 2003 (Thomsen et al., 2007a) and Swedish breast milk from 1972 to 1997 (Meironyté et al., 1999). Similar increases in PBDE concentrations in various human tissues from numerous locations between the 1980s and early 2000s have also been reported (Hites, 2004; Schecter et al., 2005; Sjödin et al., 2004). Encouragingly, following their general increase in the last two decades of the 20th century, there are signs of levelling off or decreasing concentrations of PBDEs in ringed seals from Holman Island in the western Canadian Arctic since the early 2000s (Ikonomou et al., 2002, 2005). This temporal trend is consistent with observations in some other environmental compartments as outlined in section 1.3.2.

BDE-209 was initially assumed not to be bioavailable given its high molecular weight (959 g mol^{-1}). For example, while tetra-hexa-BDEs displayed capacity for biomagnification in Arctic biota; BDE-209 was found to display only minor or no biomagnification potential (de Wit et al., 2010). However, the occurrence of BDE-209 in human blood and milk samples at considerable levels has been reported, see Table 1.4. Indeed, BDE-209 was the most abundant congener in: blood serum of workers at an electronic waste dismantling region in Guangdong,

China (Qu et al., 2007), in blood and breast milk of donors from a PBDE production area located near Laizhou Bay, China (Jin et al., 2009) and in various panda tissues (Hu et al., 2008). Closer to home, while BDE-47 (average 3.3 ng g^{-1} lw) dominated in 35 human milk samples collected from Birmingham, UK, BDE-209 was detected in 69% of samples - albeit at far lower concentrations (average 0.3 ng g^{-1} lw) (Abdallah and Harrad, 2014).

Along with PCBs, PBDEs are a suspected cause of the decline in the eel population (Tapie et al., 2011). In terms of their specific adverse health impacts, PBDEs are structurally similar to both thyroid hormones and PCBs, and their potential adverse effects in wildlife and humans include: toxic effects on sperm function, sex hormones, reproduction, thyroid hormone disruption, neurodevelopmental deficits, and carcinogenesis (Fowles et al., 1994; Tseng et al., 2006; McDonald, 2002; Hites 2004; Julander et al., 2005). In one case study, the serum levels of PBDEs, thyroid-stimulating hormone (TSH) and frequencies of micro-nucleated binucleated cells (Mned BNC) of local residents (n=23) living close to an e-waste site, who manually dismantled and "recycled" e-waste daily, were found to statistically significantly exceed those in farmers (n=26) from a control location 50 km away from the e-waste site (Yuan et al., 2008). Even more striking was that a history of working with e-waste was a significant predictor of the Mned BNC frequency, indicating the potential effect of PBDEs on levels of TSH and genotoxic damage in these workers (though no association between PBDE exposure and oxidative DNA damage was found) (Yuan et al., 2008). Significant positive associations were found between indoor dust concentrations of PBDEs and several hormone levels in men of 18-54 years age from couples seeking infertility treatment, suggesting that exposure to PBDEs via indoor dust may cause endocrine disruption in men (Johnson et al., 2013). Other effects on the endocrine system and reproductive outcomes are known. For example, in a PBDE source area, a statistically significant higher ratio of female to male births was reported (Jin et al., 2009).

Based on the available toxicological evidence, the USEPA has established oral reference doses (RfD) for PBDEs of: 7, 3, 0.1, 0.2, 2 μg kg^{-1} day^{-1} for deca-BDE, octa-BDE, tetra-BDE, hexa-BDE, and penta-BDE homologues, respectively (USEPA technical fact sheet-PBDEs and PBBs). The average exposure of a UK nursing infant to Σtri-hexa BDEs was an estimated 35 ng kg^{-1} day^{-1} via breast milk, which exceeded the upper-bound dietary intakes of both UK adults and toddlers (Abdallah and Harrad, 2014), but was about 100 times lower than the EPA RfD.

1.4 HBCDs

1.4.1 Introduction

Hexabromocyclododecane (HBCD) has been produced since the 1960s (Marvin et al., 2011) and used as an additive BFR in expanded (EPS) and extruded polystyrene (XPS) foams used as thermal insulation for buildings, as back-coating for upholstery textiles, and in electronic housing (Covaci et al., 2006; de Wit et al., 2010). Since the 1980s, the BFR industry has employed HBCD as an early replacement for Penta-BDE in Europe and more recently in the US (Muir and de Wit, 2010), making it currently the most abundantly used additive BFR. HBCD is produced in China (9,000-15,000 tons in 2009/10), Europe and the USA (combined annual 13,426 tons in 2009), and Japan (data not available), with current known annual worldwide production being approximately 28,000 tons. The main share of the market volume is in Europe and China (UNEP, SCOP-HBCD risk management evaluation); with the latest data available showing that in 2001 - in contrast to PBDEs - 60% of HBCD was consumed in Europe compared to 17% in the Americas (BSEF, 2006).

HBCD isomers possess relatively lower water solubility and vapour pressures to the 6 non-dl-PCBs (PCBs-28 to 180), with K_{OW} values similar to lower PCB congeners. Like other POPs, HBCD can release into the environment during production and manufacturing, processing, transportation, use, handling, storage or containment, and from disposal of the substance or products containing the substance, via either point source discharges or diffuse releases (UNEP, SCOP-HBCD risk management evaluation).

As a result of its persistence and potential adverse environmental and ecological impacts, HBCD has attracted the attention of legislators worldwide. It was included in the OSPAR list of chemicals for priority action under their Hazardous Substances Strategy (OSPAR, 2007). This restriction was closely followed in 2012 by its listing under the Stockholm Convention on POPs. However, time-limited exemptions were granted for its production and use in EPS and XPS building insulation foam (BSEF, 2013).

Currently, HBCD emissions are controlled via two programmes: VECAP (the Voluntary Emissions Control Action Programme) for BFRs that aims to limit use in textiles/plastics, and SECURE (Self Enforced Control of Use to Reduce Emissions) (HBCD Factsheet, BSEF, 2012) the objective of which is to minimise its use in EPS and XPS.

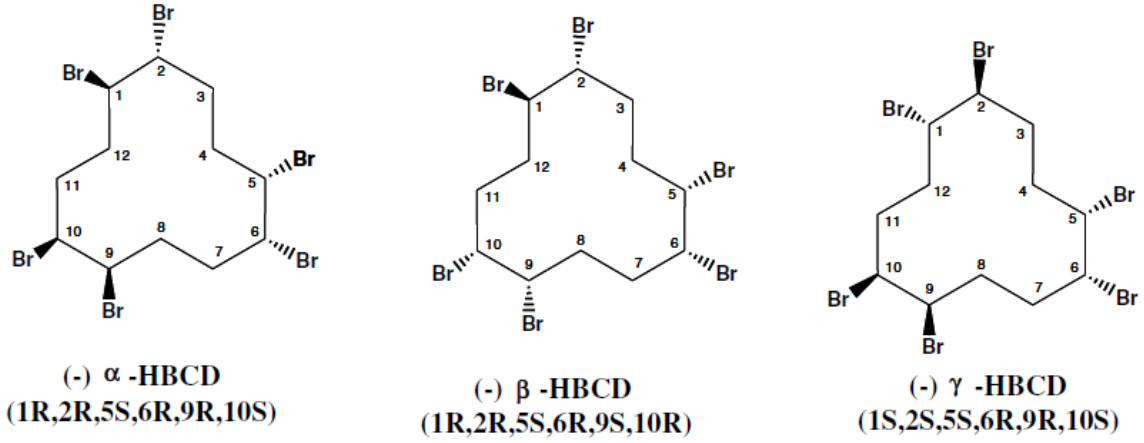


Figure 1.4 Chemical structure of α-, β-, and γ-HBCD diastereomers (from left to right)

Table 1.5 Physicochemical properties of the principal HBCD diastereomers (KEMI, 2007)

Parameter	Value
Chemical Formula	$C_{12}H_{18}Br_6$
Molecular Weight (g mol^{-1})	614.7
Melting Point (°C)	179-181 for α-HBCD 170-172 for β-HBCD 207-209 for γ-HBCD
Water Solubility (g L^{-1})	7.6 x10^{-8} for α-HBCD 2.3 x10^{-8} for β-HBCD 3.3 x10^{-7} for γ-HBCD 1.0 x10^{-7} for ΣHBCDs
Vapour Pressure (Pa, at 21°C)	6.27 x10^{-5}
Log K_{OW}	5.07 for α-HBCD 5.12 for β-HBCD 5.47 for γ-HBCD 5.62 for ΣHBCDs

1.4.2 Environmental Fate

As summarised in Table 1.6, HBCDs are now environmentally ubiquitous with their presence reported in various environmental compartments including humans. However, like PCBs and PBDEs, studies on HBCD in the UK water system are rare, and there is a striking gap in its temporal and spatial trends.

The onset of the environmental occurrence of HBCD in sediment core samples appears to have taken place mainly during the 1960s-1980s, followed by generally increasing

concentrations. Such temporal trends have been observed in many studies: e.g., in sediment cores from Switzerland (Kohler et al., 2008; Bogdal et al., 2008) and Tokyo Bay (Minh et al., 2007), as well as in archived biological samples, e.g., Californian sea lions (Stapleton et al., 2006), and guillemot eggs from the Baltic sea (Sellstrom et al., 2003). HBCD was found to have increased significantly in dolphin samples collected from Hong Kong over the period 1997-2007, while no significant temporal trends were observed for PBDEs (BDE-209 included) (Lam et al., 2009). However, conflicting trends were observed in three sediment cores from Lake Thun, Switzerland (Bogdal et al., 2008), indicating the existence of various influencing factors. Strikingly, a few studies have reported a recent decrease or levelling off in concentrations of HBCDs in archived biological samples. For example, Law et al. (2012) reported a sharp increase in HBCDs in blubber of harbour porpoise in the UK between 2000 and 2001, followed by a rapid decrease between 2003 and 2004, which the authors attributed to the closure in 2003 of an HBCD production facility in northeast England coupled with reduced HBCD sales in the UK leading up to that point. Additionally, following a peak in 2000, a significant decrease was reported in concentrations of HBCDs in herring gull eggs on three German islands (1988-2008; Esslinger et al., 2011).

Like other POPs, there is strong evidence that concentrations of HBCDs in the environment are driven by anthropogenic activities. In a study of 3 Japanese rivers (Managaki et al., 2012), HBCD levels as high as 134-2060 ng g^{-1} dw were found in sediments from a river receiving textile wastewater; while concentrations of 7.5-112 and 0.8-4.5 ng g^{-1} dw were found in sediments from urban rivers with surrounding populations of 11 and 1.8 million, respectively (Managaki et al., 2012). Consistent with this, the concentrations of HBCDs in sediment and fish samples from the Cinca River in Spain were substantially higher downstream than upstream of a heavily industrialised area (Eljarrat et al., 2004).

It is believed that HBCD has the capacity to undergo long-range environmental transport. Similar to other POPs, HBCD is easily sorbed on organic matter due to its hydrophobicity and low volatility, and enters the aquatic environment through deposition of atmospheric particles, soil erosion, surface runoff, and discharge of municipal and industrial wastewater (Remberger et al., 2004). Like PBDEs, the occurrence of HBCD in the Arctic environment, was attributed to atmospheric and pelagic transport from Western Europe and Eastern North America (de Wit et al., 2010). However, it was noted that there were higher HBCD concentrations near populated areas of the Arctic, indicating local anthropogenic influences (de Wit et al., 2010).

HBCD was found to degrade in both anaerobic and aerobic soils (Davis et al., 2005). Moreover, it was reported to display a microbial debromination half-life of 0.66 days in digested sewage sludge under anaerobic conditions (Gerecke et al., 2006). This is consistent with the hypothesis that HBCD is less persistent than PCBs and PBDEs.

While there exists a theoretical 6 diastereomers and 4 *meso* forms of HBCD; the technical HBCD mixture comprises essentially the three diastereomeric enantiomer pairs of (±) α-, (±) β-, and (±) γ-HBCD, alongside the two *meso* forms of δ-, and ε-HBCD. The relative abundance in one sample of the HBCD technical formulation was 11.8%, 5.8%, 81.6%, 0.5%, and 0.3% of ΣHBCDs for α-, β-, γ-, δ-, and ε-HBCD respectively (Heeb et al., 2005). Among those isomers, α-, β-, γ-HBCD were most frequently detected in fish samples from English lakes, with δ-HBCD also detected at up to 11% ΣHBCDs in some samples (Harrad et al., 2009). The HBCD diastereomer pattern can vary between and within environmental compartments. While either γ-HBCD or α-HBCD dominates in the atmosphere (Hoh and Hites, 2005), aquatic biota samples (Zegers et al., 2005; de Wit et al., 2010; Zhang et al., 2009a; Asante et al., 2013) and human samples are usually dominated by α-HBCD (Roosens et al., 2009; Abdallah and Harrad, 2011; Carignan et al., 2012; Shi et al., 2013; Lankova et al., 2013), γ-HBCD usually dominates in sediment samples (Managaki et al., 2012; Guerra et al., 2009; Morris et al., 2004; Zhang et al., 2009a; La Guardia et al., 2013), and also air conditioning filter dust (Ni and Zeng, 2013). With respect to indoor dust, variation exists between studies. In indoor dust from urban Romania, α-HBCD dominated consistently (80-97% ΣHBCDs) (Dirtu et al., 2012), a profile generally consistent with that in Belgian dust (D'Hollander et al., 2010); but in contrast with that in UK dust where greater relative abundance of γ-HBCD was observed (Abdallah et al., 2008; Harrad et al., 2010).

Such variations in HBCD isomer patterns are plausible given the potential enrichment of α-HBCD caused by thermal stereoisomerisation at temperatures above 190 °C (Peled et al., 1995) which could occur during incorporation of HBCD into polymers. Additional explanations include the more facile metabolism of β- and γ-HBCD than α-HBCD in biological organisms (Zegers et al., 2005), the relatively stronger biomagnification potential of α-HBCD (de Wit et al., 2010), and the greater environmental persistence of α-HBCD compared to β- and γ-HBCD (Gerecke et al., 2006).

Table 1.6 A summary of ΣHBCD concentrations in the environment, wildlife and humans (mean values in parentheses)

Matrix	Description	Concentration	Reference
Outdoor air (pg m^{-3})	Background areas, Sweden (2000/1)	<0.001-0.28	Remberger et al., 2004
	Urban areas, Sweden (2000/1)	0.076; 0.61	
	Production of flame retarded XPS plastics, Sweden (2000)	1070	
	Landfill for construction and demolition waste, Sweden (2000/1)	0.013; 0.18	
	Textile industry, Sweden (2000/1)	0.019; 0.74	
	East-Central US	0.16-11	Hoh and Hites, 2005
Air deposition (ng m^{-2} day^{-1})	Background areas, Sweden (2000/1)	0.02-13	Remberger et al., 2004
	Urban areas, Sweden (2000/1)	5.5; 366	
Indoor air (pg m^{-3})	Offices, UK	70-460 (180)	Abdallah et al., 2008
	Homes, UK	67-1300 (250)	
	Public microenvironments, UK	820-960 (900)	
	Air conditioning filter dust taken as particulate phase, office building, Shenzhen, China (2009)	652-122973 ng g^{-1}	Ni and Zeng, 2013
Indoor dust (ng g^{-1})	Homes, UK (2007)	228-140774	Abdallah and Harrad, 2009
	Offices, UK (2007)	279-4004	
	Cars, UK (2007)	194-55822	
	Belgium (2007)	33-758 (160)	Roosens et al., 2009
	Floor and mattress dust, Rural and urban New Zealand	<2-4100	Ali et al., 2012
	Vacuum bag, US (2002/3)	n.d.-1999 (197)	Johnson et al., 2013
	Main living areas, greater Boston, MA area, US (2006)	<4.5-130200 (354)	Stapleton et al., 2008
	Bedrooms, greater Boston, MA area, US (2006)	<4.5-9710 (144)	
	Home vacuum bags, greater Boston, MA area, US (2006)	21.0-35100 (282)	
	Home vacuum bags, greater Boston, MA area, US (2002-7)	<2-2750 (166)	Stapleton et al., 2009
	Eastern Romania	Median 250	Dirtu et al., 2012
Water (pg L^{-1})	9 English lakes throughout England (2008/9)	80-270	Harrad et al., 2009
	Freshwater, Denmark (2012)	96-2900	Vorkamp et al., 2014
	Sea water, Denmark (2012)	52-400	
	Landfill leachate, landfill for construction and demolition waste, Sweden (2000/1)	3000; 9000	Remberger et al., 2004
	Waste water, washing of textiles, Sweden (2000)	31000	
	Dissolved phase, Dongjiang River, South China (2010)	9.5-82.4 (39.7)	He et al., 2013
	Particulate phase, Dongjiang River, South China (2010)	n.d.-11.3 (8.0) (ng g^{-1} dw)	

Matrix	Description	Concentration	Reference
Water (pg L^{-1})	E-waste recycling site, south China (2006)	Average 60 (n=6)	Wu et al., 2010
	Taihu Lake, China	n.d.-370	Xu et al., 2013
Soil (ng g^{-1} dw)	300-700 m away from a XPS factory, Sweden (2000)	140-1300	Remberger et al., 2004
	Belgiaum(2006/7)	<0.1-6.6	Covaci et al., 2009
Sediment (ng g^{-1} dw)	9 English lakes	0.88-4.8	Harrad et al., 2009
	Textile industry, Sweden (2000/1)		Remberger et al., 2004
	Lake Greifensee, Sweden (2003)	2.5	Kohler et al., 2008
	North Sea Estuaries, Netherland	<0.8-9.9 (3.2)	Morris et al., 2004
	North Sea Estuaries, Dublin Bay, Ireland	<1.7-12 (3.3)	
	Up-and downstream of a heavily industrialised town, Cinca River, Spain	n.d.-514	Eljarrat et al., 2004
	Great Lakes	0.04-3.1	Yang et al., 2012
	San Francisco Bay	0.1-1.7	Klosterhaus et al., 2012
	Durban Bay and 13 rivers, South Africa (2011)	n.d.-27500 (1800) ng g^{-1} TOC	La Guardia et al., 2013
	Tsurumi River, an urban river, Japan (2008)	0.8-4.8	Managaki et al., 2012
	Yodo River, an urban river, Japan (2008)	7.5-112	
	Kuzuryu River, receiving textile wastewater, Japan (2008)	134-2057	
	2 streams in an e-waste site, China	4.6-35 (11)	Zhang et al., 2009a
	7 major river drainage basins, China (2003/4)	n.d.-206	Li et al., 2013
	Dongjiang River, South China (2009)	0.07-31.6 (6.9)	He et al., 2013
	Taihu Lake, China	0.046-2.56	Xu et al., 2013
	E-waste recycling site, south China (2006)	Average 169 ng g^{-1} ww	Wu et al., 2010
	Downstream, Dongjiang River, South China (2009)	<2.5-424	Zhang et al., 2011b
Sewage Sludge (ng g^{-1} dw)	Digested sludge, sewage treatment plants, Sweden (2000)	<1	Remberger et al., 2004
	Primary sludge, sewage treatment plant, Sweden (2000)	6.9	
	Washing of textiles, Sweden (2000)	30; 33	
	17 wastewater treatment plants, Catalonia, Spain (2009)	nd-97.5 (19.3)	Gorga et al., 2013
Aquatic invertebrate, fish and mammals (ng g^{-1} lw)	Herring muscle, marine background, Sweden (1999-2000)	21-58	Remberger et al., 2004
	Baltic herring muscle, marine background, Sweden (1999)	34-180	
	Up-/ down-stream a sewage treatment plants, river Viskan, Sweden	65-1800	Remberger et al., 2004
	Fish muscle tissue and liver, up-and downstream of a heavily industrialised town, Cinca River, Spain	n.d.-750 (ng g^{-1} ww)	Eljarrat et al., 2004
	Fish, Denmark (2012)	n.d.-0.056	Vorkamp et al., 2014
	Bottlenose dolphin, US	0.46-72.6	Johnson-Restrepo et al., 2008
	Bull shark, US	9.15-413	

Matrix	Description	Concentration	Reference
Aquatic invertebrate, fish and mammals (ng g^{-1} lw)	Atlantic sharpness shark, US	1.83-156 (54.5)	Johnson-Restrepo et al., 2008
	Fish, San Francisco Bay (2006)	2.5-24.7	Klosterhaus et al., 2012
	Seal blubber, adults, San Francisco Bay (2007/8)	4.4-19.3	
	Seal blubber, pups, San Francisco Bay (2007/8)	2.0-11.7	
	Three tilapia fish species, lakes, pond, lagoons, Ghana (2010)	<0.01-8.5	Asante et al., 2013
	Winkle from 2 streams in an e-waste site, China	123-333 (175)	Zhang et al., 2009a
	Crucian carp from 2 streams in an e-waste site, China	199-728 (339)	
	Loach from 2 streams in an e-waste site, China	934-3529 (1620)	
	Cetacean samples, Hong Kong, China (2002-8)	4.1-519	Lam et al., 2009
	Limnic and marine cohorts, Tianjin, China (2011)	64.3-1111	Zhang et al., 2013
	Mud carp, Dongjiang River, South China	17.5-154 (58.3)	He et al., 2013
	Nile tilapia, Dongjiang River, South China	n.d.-391 (92)	
	Plecostomus, Dongjiang River, South China	n.d.-832 (361)	
Chicken faeces (ng g^{-1} dw)	Belgian (2006/7)	<0.1-23.9	Covaci et al., 2009
Food	Market basket study, UK	0.02-0.30 ng g^{-1} ww	Driffield et al., 2008
	Chicken eggs, Belgian home-produced eggs (2006/7)	<0.4-62 ng g^{-1} lw	Covaci et al., 2009
	Belgian duplicate diet (2007)	<0.01-0.35 ng g^{-1} ww	Roosens et al., 2009
Human adipose tissue (ng g^{-1} lw)	New York, USA (n=20, 2003-4)	<0.0026-2.41 (0.333)	Johnson-Restrepo et al., 2008
Human milk (ng g^{-1} lw)	General population, Birmingham, UK (n=34)	1.04-22.37 (5.95)	Abdallah and Harrad, 2011
	Olomouc region, Czech Republic (2010)	<1-76	Lankova et al., 2013
	Urban/suburban Beijing, China (n=103, 2011)	n.d.-78.28 (4.29)	Shi et al., 2013
Human blood serum (ng g^{-1} lw)	Dutch mothers	<0.160-7 (1.1)	Weiss et al., 2004
	Norway	6-856 (190)	Thomsen et al., 2007b
	Norway	<1.0-52	Thomsen et al., 2008
	Swedish mothers (pmol g^{-1} lw, pool sample, 2004)	0.6	Fängström, et al., 2008
	Belgian adults, 20-25 years of age (n=16)	<0.5-11.3 (2.9)	Roosens et al., 2009

1.4.3 Human Exposure and Adverse Health Effects

As summarised in Table 1.6, HBCD has been found in almost all environment compartments with considerable concentrations found in aquatic organisms and foodstuffs, providing evidence of its bioaccumulative capacity. Harrad et al., (2009) reported an average bioaccumulation factor (BAF) of 2,100 for ΣHBCDs, with higher values observed for α-HBCD (5,900), than β- (1,300) and γ-HBCD (810). Moreover, food web magnification was reported for α-HBCD and ΣHBCDs, with trophic magnification factors of 2.22, and 1.82, respectively (Wu et al., 2010), indicating both the potential for biomagnification, and its isomer-specificity. Similarly, α-HBCD biomagnified in Arctic food webs (de Wit et al., 2010), with higher contamination levels found in marine top predators than in lower terrestrial organisms, causing further concerns about the accumulation and potential adverse effects on biota, including humans. The wide presence of HBCD has been reported in human adipose tissue, blood serum, and milk samples, as summarised in Table 1.6. Alarmingly, the detection frequency of HBCD was as high as 90% in the livers of foetuses of gestation ages 6.5-19.5 weeks (<1-4500 ng g^{-1} lw; n=52) and 97% in associated placental tissues (<1-5600 ng g^{-1} lw; n=142) collected between 1998-2010 in Canada (Rawn et al., 2014).

The pathways of human exposure to HBCD are assumed similar to those for PBDEs. The major exposure pathways of the general public to HBCD are now recognised as comprising indoor dust ingestion (Roosens et al., 2009; Abdallah and Harrad, 2009) the consumption of contaminated food (Driffield et al., 2008), and for infants, breast milk (Abdallah and Harrad, 2011). In a study of human milk from mothers in Boston, USA; HBCD levels were found significantly positively associated with the number of electronics in the home, and reduced in participants who regularly chose organic foods compared to those who did not, suggesting that lifestyle factors such as demographic, dietary and behavioural habits are related to body burdens of HBCD, and that domestic electronics may be an important source of HBCD exposure in the indoor environment (Carignan et al., 2012). Estimates of personal exposure to HBCDs via ingestion of indoor dust for 21 UK adults were 4.5-1851 and 11-4630 ng day^{-1} under an average and a high dust ingestion scenario, respectively (Abdallah and Harrad, 2009). Correlation between HBCD concentrations in serum from 16 Belgian adults (aged 20-25) and their exposure via indoor dust, but not via dietary ingestion has been reported (Roosens et al., 2009), indicating the important role of dust ingestion to HBCD exposure. In contrast, general UK population intakes of HBCD via inhalation, indoor dust ingestion (based on mean dust

intake), indoor dust ingestion (based on high dust intake), and diet, were estimated at 5.0, 132, 329, and 413 ng day^{-1} respectively for adults, and 1.0, 404, 1473, and 240 ng day^{-1} respectively for toddlers (Abdallah et al., 2008). This was interpreted as indicating that for adults, dietary exposure (75%) was the principal contributor to the exposure to HBCD of general UK population, followed by indoor dust ingestion (24%). However, for toddlers, indoor dust ingestion (63%) appears more important than dietary exposure (37%) (Abdallah et al., 2008). Moreover, concentrations of HBCDs in the blood serum of consumers of fish from Lake Mjosa were significantly higher than those of a reference group of Norwegians eating only food with background levels of contamination (Thomsen et al., 2008); and good agreement was observed between measured HBCD body burdens and those predicted by a pharmacokinetic model to arise from exposure via dust, diet and air (Abdallah and Harrad, 2011). For both adults and toddlers inhalation exposure was shown to be a minor pathway (<1%) (Abdallah et al., 2008).

Animal studies indicated that oral exposure to HBCDs induces hepatic cytochrome P450 (CYP) enzymes in rats, with certain CYP inductions being more pronounced in females (Germer et al., 2006). Some early observations indicate that HBCD exposure could cause neurobehavioral alterations in adult mice (Eriksson et al., 2006), and display adverse effects on the liver and thyroid hormone system in wistar rats (van der Ven et al., 2006). Another study reported that indoor dust concentrations of HBCD were associated with decreased sex hormone binding globulin (SHBG) levels and an increased free androgen index in a cohort of men aged between 18 and 54; suggesting that exposure to HBCD via indoor dust may cause endocrine disruption in men (Johnson et al., 2013). HBCD has undergone an EU Risk Assessment (RA) for environment and human health over the period 1996-2008. HBCD was identified as posing no risk to consumers, with no risk observed to workers when standard industrial hygiene measures (current EU practice) are applied. However, the same RA concluded that HBCD has PBT properties, and noted concerns about its increasing concentrations in the environment. Of note, is HBCD's classification as a H410 substance, signifying that it is very toxic to aquatic organisms and may cause long term adverse effects in aquatic environment.

1.5 NBFRs

1.5.1 Introduction

The so-called novel/alternative BFRs (NBFRs) have been recently defined as those BFRs

either new to the market or newly/recently observed in the environment (Covaci et al., 2011). Total global NBFR production has been estimated at 100,000-180,000 tons annually (Harju et al., 2009). In this study, those NBFRs that have been studied to a limited degree and their occurrence reported in a variety of environmental matrices, are of particular interest. To be specific, they are: Bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), Decabromodiphenylethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), TBBPA-dibromopropyl ether (TBBPA-DBPE), Pentabromoethylbenzene (PBEB), and Hexachlorocyclopentadienyldibromocyclooctane (HCDBCO). See Table 1.7 for their physicochemical properties and Figure 1.5 for their chemical structures.

Table 1.7 Physicochemical properties of some major NBFRs (Covaci et al., 2011)[a] in this study

Compound	Molecular Formula	Molecular Weight	Vapour Pressure (Pa, at 21°C)	Water Solubility (g L^{-1})	Log K_{OW}
TBPH	$C_{24}H_{34}Br_4O_4$	706.1	1.55×10^{-11}	1.60×10^{-6}	10.08
PBEB	$C_8H_5Br_5$	500.7	3.2×10^{-4}	3.5×10^{-4}	6.40
DBDPE	$C_{14}H_4Br_{10}$	971.2	6.0×10^{-15}	2.10×10^{-7}	11.1
BTBPE	$C_{14}H_8Br_6O_2$	687.6	3.88×10^{-10}	1.90×10^{-5}	7.88
TBBPA-DBPE	$C_{21}H_{20}Br_8O_2$	943.6	1.60×10^{-7}	1.6×10^{-7}	10.42
HBB	C_6Br_6	551.5	1.14×10^{-4}	7.70×10^{-4}	5.85

[a] Data from SciFinder originating from calculated properties (ACD/lab Software V9.04)

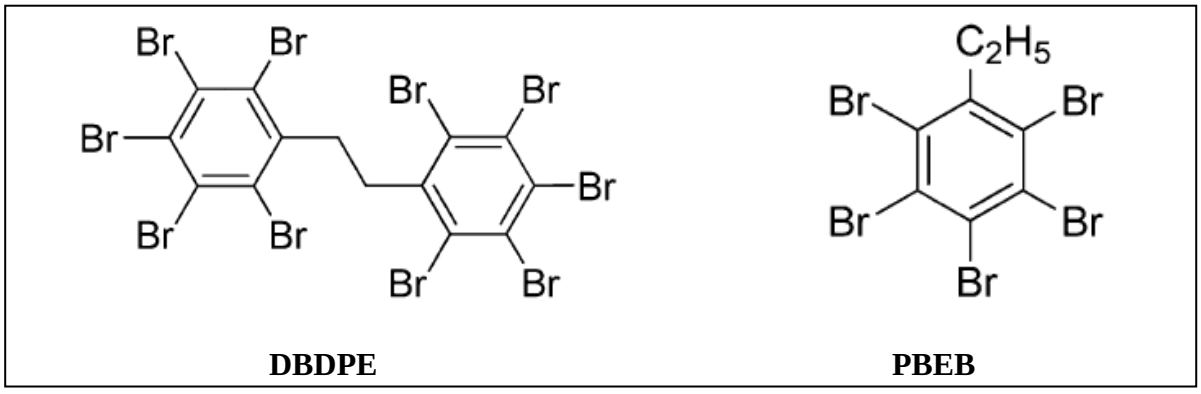
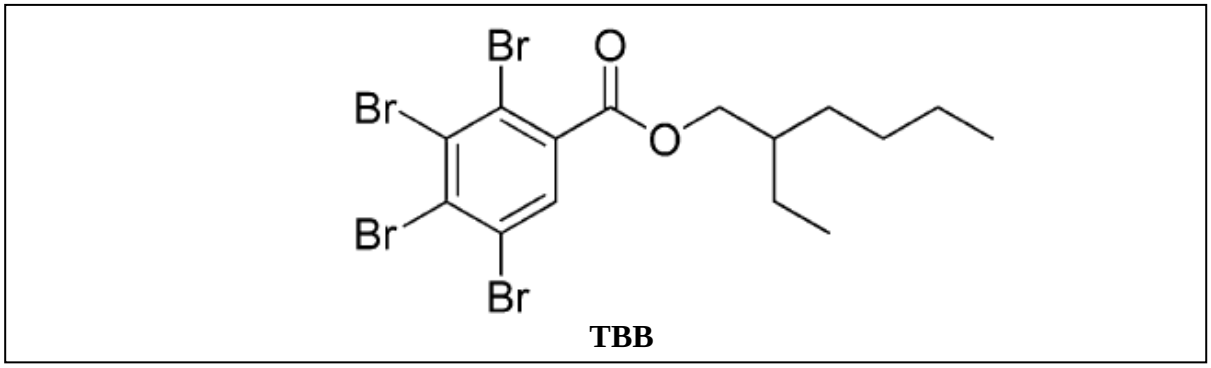
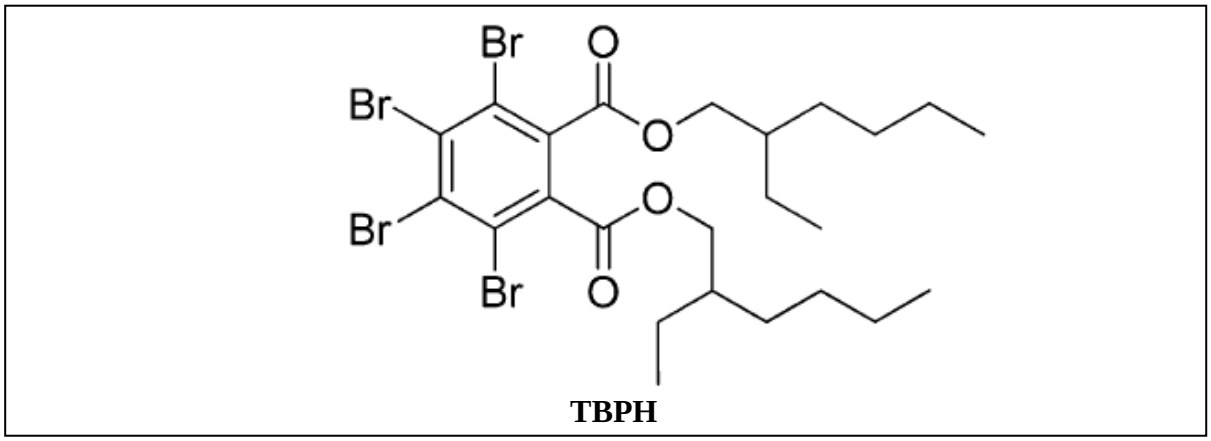


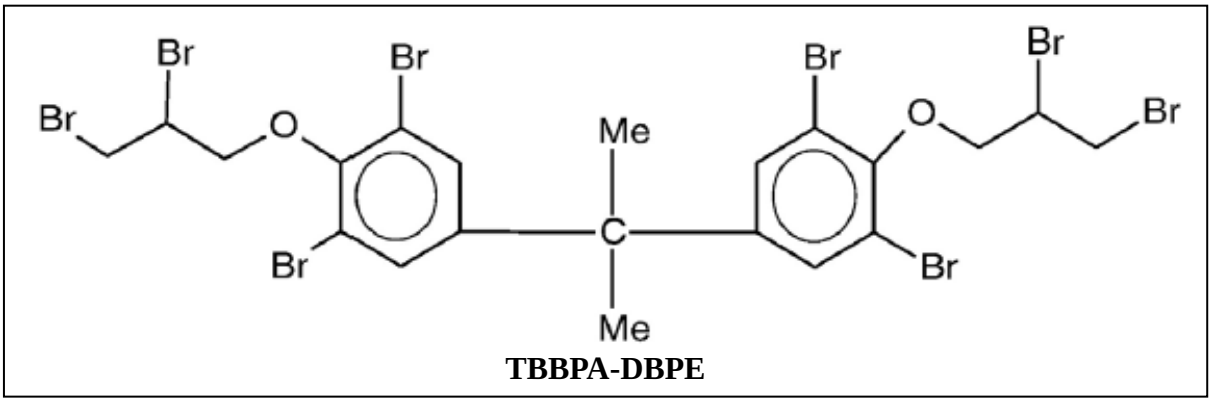
Figure 1.5 Part 1: Chemical structures of DBDPE, PBEB, and BTBPE



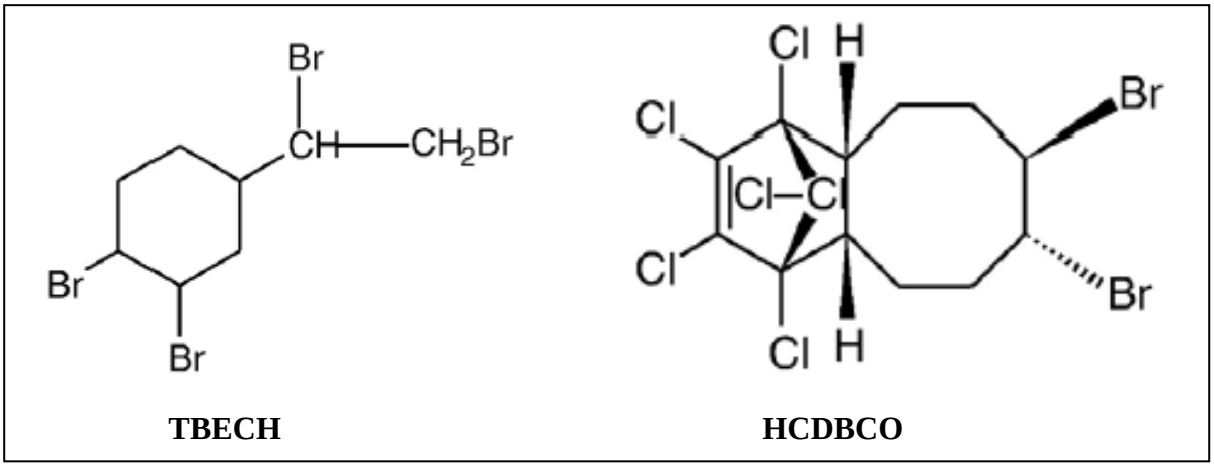
TBB



TBPH



TBBPA-DBPE



TBECH **HCDBCO**

Figure 1.5 Part 2: Chemical structures of TBB, TBPH, TBBPA-DBDPE, TBECH, and HCDBCO

1.5.2 Environmental Fate

Information on the environmental presence, trends, fate and behaviour of NBFRs is scarce. Notwithstanding this, current knowledge about their production, physicochemical properties, analytical chemistry, levels of environmental contamination, exposure pathways, and potential toxicity has been reviewed recently in a number of publications (Papachlimitzou et al., 2012; Covaci et al., 2011; Luo et al., 2010; de Wit et al., 2010).

As summarised in Table 1.8-1.13, though studies on NBFRs are relatively limited so far, they have been detected in various indoor and outdoor environmental compartments. As a result of restrictions/bans on the production and use of "legacy" BFRs such as PBDEs and HBCDs, it is believed the demand for NBFRs has increased and will continue to increase to meet flammability standards. One observation supporting this hypothesis is the noticeable increase in the levels of TBBPA-DBPE and DBDPE observed in recent sediments from the Pearl River Delta, with concentrations even exceeding those of BDE-209 in some samples (Shi et al., 2009).

While relatively high concentrations of DBDPE and TBBPA-DBPE were found in the Pearl River Delta (PRD) environment generally, concentrations of BTBPE were higher in areas impacted by e-waste treatment; suggesting industrial activities and the recycling of e-waste in the PRD have introduced distinct patterns of BFR contamination (Shi et al., 2009). BTBPE and DBDPE concentrations were both highest in indoor dust from e-waste workshops, followed by concentrations in dust from e-waste impacted areas for BTBPE but from urban areas for DBDPE (Zheng et al., 2011). Evidence of the impact of diffuse anthropogenic emissions was provided by Ma et al. (2013), who reported that the concentrations of BTBPE, TBB, TBPH, and DBDPE were related to the number of people living within a 25 km radius of the sampling site in air and precipitation samples from a number of North American locations.

An important observation is that NBFRs like TBECH, BTBPE, PBEB, PBT, and PBBs, have been detected in the Arctic environment (de Wit et al., 2010), providing evidence of their capacity for long-range environmental transport. While certain NBFRs have similar K_{OW} values to PCBs and many PBDEs; TBPH, DBDPE and TBBPA-DBPE possess markedly higher K_{OW} values (see Table 1.7) that slightly exceed that of BDE-209, suggesting potentially similar environmental fate and behaviour, including bioaccumulation potential. Moreover, the high molecular weights and low vapour pressures of TBPH and DBDPE suggest limited

potential for atmospheric transport, akin to BDE-209.

1.5.2.1 Environmental Fate of TBPH and TBB

In 2006, the production/import volume of TBPH in the US was 500-5000 tons (USEPA Inventory Update Reporting). TBB and TBPH are both active ingredients of the commercial flame retardant product Firemaster 550 (FM 550), which was introduced in 2003 by Chemtura as an alternative to Penta-BDE (Stapleton et al., 2008). In addition to its application in FM-550, TBPH has a comprehensive range of other applications as a BFR in materials such as: wire and cable insulation, film and sheeting, carpet backing, coated fabrics, wall coverings, and adhesives (http://www.chemtura.com); and as a plasticiser in polyvinyl chloride (PVC) and neoprene (Andersson et al., 2006). This much wider range of applications for TBPH provides a highly plausible explanation for the enrichment of TBPH relative to TBB in environment and biota samples, compared to their relative abundance in FM 550. The ratio of TBB:TBPH in FM 550 mixture has been reported as 3:1 (Ma et al., 2013) and 4:1 (Stapleton et al., 2008). By comparison, the average TBB:TBPH ratio was 4.4 (range 0.05-50) in US indoor dust (Stapleton et al., 2008), 0.4 (range 0.01-3.8, median 0.15) in Romanian dust (Dirtu et al., 2012), and 0.81 in US air (Ma et al., 2013). The TBB:TBPH ratio in environmental matrices will also be influenced by the relative environmental fate and behaviour of the two chemicals.

Stapleton et al. (2008) reported the occurrence of TBB and TBPH in US home dust, making it the first report of their presence in indoor dust; with Ali et al. (2011a) reporting their concentrations for the first time in European indoor dusts. The occurrence of TBB and TBPH in marine mammals was first reported in 2009 in a study in dolphins from Hong Kong (Lam et al., 2009), while the non-detection of TBB and TBPH in San Francisco Bay sediments was attributed by the authors to matrix interferences (Klosterhaus et al., 2012). Moreover, TBPH has only been targeted occasionally in studies of NBFRs to date. This is likely an important omission as burgeoning use of TBPH in North America is indicated by its increasing concentrations in air (doubling time ~2 years) at three out of five monitored sites in the Great Lakes region over the period 2005-2011 (Ma et al., 2013).

Table 1.8 Summary of concentrations of TBPH in various environmental matrices (mean values in parentheses)

Matrix	Description	Concentration	Reference
Outdoor Air (pg m^{-3})	Five sites, Great Lakes region	0.5-8.0 (averaged over the years 2005-11)	Ma et al., 2013
Indoor Dust (ng m^{-3})	Classrooms, West Midlands, UK (2007-8)	<2-6175 (381)	Ali et al., 2011a
	Homes, Antwerp, Belgium (2008)	<2-5004 (212)	
	Offices, Antwerp, Belgium (2008)	16-265 (95)	
	Floor and mattress dust, Rural and urban New Zealand	<2-640	Ali et al., 2012
	Vacuum bag, US (2002/3)	n.d.-47110 (377)	Johnson et al., 2013
	Main living area, greater Boston, MA area, US (2006)	3.0-10630 (234)	Stapleton et al., 2008
	Bedroom, greater Boston, MA area, US (2006)	1.5-763 (105)	
	Home vacuum bag, greater Boston, MA area, US (2006)	24.3-111 (65.8)	
	Various Thai e-waste facilities	79-1300 (270) median 180	Ali et al., 2011b
	Eastern Romania	median 20	Dirtu et al., 2012
Sediment (ng g^{-1} dw)	San Francisco Bay (2007)	<0.20	Klosterhaus et al., 2012
	Durban Bay and 13 rivers, South Africa (2011)	n.d.- 899 (96) ng g^{-1} TOC	La Guardia et al., 2013
Biota (ng g^{-1} lw)	Cormorant eggs, San Francisco Bay (2008)	<12	Klosterhaus et al., 2012
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Seal blubber, adults, San Francisco Bay (2007/8)	Not reportable	Klosterhaus et al., 2012
	Seal blubber, pups, San Francisco Bay (2007/8)	Not reportable	
	Cetacean samples, Hong Kong, China (2002-8)	<0.04-3859	Lam et al., 2009

Table 1.9 Summary of concentrations of TBB in various environmental matrices (mean values in parentheses)

Matrix	Description	Concentration	Reference
Outdoor Air (pg m^{-3})	Five sites, Great Lakes region	0.4-4.3 (averaged over the years 2005-11)	Ma et al., 2013
Indoor Dust (ng m^{-3})	Classrooms, West Midlands, UK (2007-8)	<2-289 (45)	Ali et al., 2011a
	Homes, Antwerp, Belgium (2008)	<2-436 (20)	
	Offices, Antwerp, Belgium (2008)	<2-31 (12)	
	Floor and mattress dust, Rural and urban New Zealand	<2-2285	Ali et al., 2012
	Eastern Romania	median 5	Dirtu et al., 2012
	Vacuum bag, US (2002/3)	n.d.-72460 (409)	Johnson et al., 2013
	Main living area, greater Boston, MA area, US (2006)	<6.6-15030 (322)	Stapleton et al., 2008
	Bedroom, greater Boston, MA area, US (2006)	<10.6-378 (90.4)	
	Home vacuum bag, greater Boston, MA area, US (2006)	35.7-669 (91.1)	
	Various Thai e-waste facilities	<2-59 (18) median 13	Ali et al., 2011b
Sediment (ng g^{-1} dw)	River Arga, Nalón, and Besós, Spain (2012)	n.d.	Cristale et al., 2013
	San Francisco Bay (2007)	<0.01	Klosterhaus et al., 2012
	Durban Bay and 13 rivers, South Africa (2011)	n.d.- 13900 (545) ng g^{-1} TOC	La Guardia et al., 2013
Birds (ng g^{-1} lw)	Cormorant egg, San Francisco Bay (2008)	< 8.0	Klosterhaus et al., 2012
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Blubber of harbour porpoises, UK (2008)	<0.61-3.44 (ng g^{-1} ww)	Law et al., 2013
	White croaker, San Francisco Bay (2006)	<30	Klosterhaus et al., 2012
	Shiner surfperch, San Francisco Bay (2006)	<203	
	Seal blubber, adults, San Francisco Bay (2007/8)	<1.0	
	Seal blubber, pups, San Francisco Bay (2007/8)	<1.0	
	Cetacean samples, Hong Kong, China (2002-8)	<0.04-70	Lam et al., 2009

1.5.2.2 Environmental Fate of BTBPE

BTBPE was introduced onto the BFR market in the mid-1970s and found moderate use in the early 2000s (Hoh et al., 2005) as a replacement for Octa-BDE. Its major applications were in high-impact polystyrene, acrylonitrile butadiene styrene, thermoplastic, thermoset resins, polycarbonate and coatings (Covaci et al., 2011) used in electronics like telephones, dashboards, refrigerators, and toys, etc. (Harju et al., 2009). Between 1986 and 1994, Great Lakes Chemicals produced 4,500-22,500 tons annually, a figure that decreased to 450-4,500 t after 1998 (USEPA Inventory Update Rule 2002). By 2006, the production/import volume of BTBPE in the USA was an estimated 500-5000 tons (USEPA Inventory Update Reporting).

BTBPE has been detected in sediment core slices from the Great Lakes dating from the late 1970s/early 1980s (Qiu et al., 2007; Hoh et al., 2005), and increased rapidly with a doubling time of ~2 years (Hoh et al., 2005). Between 2005 and 2011, BTBPE concentrations in North American outdoor air were either decreasing or stable (Ma et al., 2013). To our best knowledge, there exists no other information about recent temporal trends of BTBPE.

Table 1.10 Summary of concentrations of BTBPE in various environmental matrices (mean values in parentheses)

Matrix	Description	Concentration	Reference
Outdoor Air (pg m^{-3})	Sweden	<3	Sjödin et al., 2001
	Various sites, US	2.8-70	Hoh et al., 2005
	East-central US	0.025-70	Hoh and Hites, 2005
	Five sites, Great Lakes region	0.4-1.8	Ma et al., 2013
	Pearl River Delta, Southern China (2007)	3.83-67.4	Shi et al., 2009
Indoor Air (ng m^{-3})	E-waste recycling plant, Sweden	5.6-150	Sjödin et al., 2001
	Working environment, assembly of circuit boards, Sweden	<3-41 (n=6)	
	Office with computers, Sweden	<3-5.8(n=4)	
	Computer repair, Sweden	<3; 11 (n=2)	
	Teaching hall, Sweden	3; 4.8 (n=2)	
	Dismantlers, electronic recycling facility, Sweden	1.1-39 (15)	Pettersson-Julander et al., 2004
	Other workers, electronic recycling facility, Sweden	1.7-16.0 (5.2)	
	Unexposed, electronic recycling facility, Sweden	0.6-0.9 (0.8)	
Indoor Dust (ng m^{-3})	Homes, UK	n.d.-1900 (120)	Harrad et al., 2008a
	Offices, UK	n.d.-40 (7.2)	
	Cars, UK	n.d.-29 (7.7)	
	Classrooms, West Midlands, UK (2007-8)	<0.5-1741 (78)	Ali et al., 2011a
	Homes, Antwerp, Belgium (2008)	<0.5-1019 (33)	
	Offices, Antwerp, Belgium (2008)	2-384 (80)	
	Floor and mattress dust, Rural and urban New Zealand	<2-175	Ali et al., 2012
	Eastern Romania	median 5	Dirtu et al., 2012
	Vacuum bag, US (2002/3)	maximum 953(22)	Johnson et al., 2013
	Main living area, greater Boston, MA area, US (2006)	4.7-654 (48.1)	Stapleton et al., 2008
	Bedroom, greater Boston, MA area, US (2006)	1.6-789 (47.8)	
	Home vacuum bag, greater Boston, MA area, US (2006)	2.5-219 (17.7)	
	Various Thai e-waste facilities	3-22600 (7810)	Ali et al., 2011b
	Ground close to e-waste dismantling workshops, southern China (2006)	14.6-232	Shi et al., 2009
	E-waste workshop, south China	71.4-839 (297)	Zheng et al., 2011
	Resident in e-waste recycling area, south China	26.2-239 (55.7)	
	Urban area, south China	n.d.-211 (6.47)	
	Rural area, south China	6.15-19.5 (16.6)	
Water (pg L^{-1})	E-waste recycling site, south China (2006)	Average 20 (n=6)	Wu et al., 2010

Matrix	Description	Concentration	Reference
Soil (ng g^{-1} dw)	Farmland, Pearl River Delta, Southern China (2007)	0.02-0.11	Shi et al., 2009
	E-waste Processing area, Southern China (2006)	0.07-6.19	
Sediment (ng g^{-1} dw)	River Arga, Nalón, and Besós, Spain (2012)	n.d.	Cristale et al., 2013
	San Francisco Bay	<0.03-0.06	Klosterhaus et al., 2012
	Durban Bay and 13 rivers, South Africa (2011)	n.d.- 616 (34) ng g^{-1} TOC	La Guardia et al., 2013
	E-waste recycling site, south China (2006)	Average 4554 ng g^{-1} ww (n=6)	Wu et al., 2010
	Pearl River Delta, Southern China (2002/6)	0.05-21.9	Shi et al., 2009
	Pearl River Delta, Southern China (2007)	0.31-1.66	Shi et al., 2009
Birds (ng g^{-1} lw)	Muscle, Liver, Kidney, E-waste Processing area, China	0.07-2.41	Shi et al., 2009
	Eggs, Great Lakes	0.38-7.36	Gauthier et al., 2007
	Cormorant egg, San Francisco Bay (2008)	<2.0	Klosterhaus et al., 2012
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Muscle and liver of juvenile sole, French coast (2007-9)	<n.d.-72.4 (pg g^{-1} ww)	Munschy et al., 2011
	White croaker, San Francisco Bay (2006)	<3.0	Klosterhaus et al., 2012
	Shiner surfperch, San Francisco Bay (2006)	<20	
	Seal blubber, adults, San Francisco Bay (2007/8)	<0.1	
	Seal blubber, pups, San Francisco Bay (2007/8)	<0.1	
	Fish muscle tissues and livers, e-waste processing area, China	< 0.012-0.15	Shi et al., 2009
Food (ng g^{-1} lw)	UK and Irish foods (meat, meat products, offal, fish, and fish products)	<0.01-1.76	Fernandes et al., 2010
Human tissues (ng g^{-1} dw)	Hair, e-waste workshop, south China	0.15-29.2 (1.21)	Zheng et al., 2011
	Hair, resident in e-waste recycling area, south China	n.d.-5.80 (0.60)	
	Hair, urban area, south China	n.d.-2.55 (0.10)	
	Hair, rural area, south China	n.d.-1.69 (0.12)	
Toys (ng g^{-1})	Toys purchased from South China	Median 101	Chen et al., 2009

1.5.2.3 Environmental Fate of DBDPE

DBDPE was introduced in the mid-1980s (UBA, 2001) and from the early 1990s found use as an alternative to Deca-BDE (Arias, 2001) due to its similar structure to BDE-209 (Kierkegaard et al., 2004). DBDPE was mainly used as a Deca-BDE replacement in high-impact polystyrene, acrylonitrile butadiene styrene, polypropylene, and textiles (Covaci et al., 2011). Known DBDPE producers are Albemarle Corporation and some chemical corporations in China. The production volume in China in 2006 was an estimated 12,000 tons (http://www.soci.com.cn), a figure estimated to be increasing at up to 85% annually (http://www.taixinghuagong.com/). The production/import volume of DBDPE in the US in 2006 was an estimate 500-5000 tons (USEPA Inventory Update Reporting).

Compared with other NBFRs, the environmental presence and fate of DBDPE has been subject to comparatively greater study. The first detection of DBDPE in sediment cores from the Great Lakes was reported to occur 10-20 years later than the initial detection of BDE-209 (Yang et al., 2012). Despite this relatively late arrival on the market, DBDPE appears to be environmentally ubiquitous (see Table 1.11), and was the dominant NBFR detected in house dust samples (n=47) collected from Iasi, Eastern Romania (Dirtu et al., 2012). Moreover, Stapleton et al. (2008) reported a similar dominance of DBDPE in US indoor house dust, with concentrations exceeding those of TBPH and TBB; while in UK house dust, DBDPE and TBPH were the major NBFRs (Ali et al., 2011a).

While DBDPE was found in sediments from the Spanish rivers Llobregat, Anoia and Besós (Guerra et al., 2010; Cristale et al., 2013) at concentrations lower than BDE-209; it was the only NBFR detected out of 11 targeted NBFRs in the River Besós (Cristale et al., 2013). The estimated accumulation of DBDPE in sewage sludge produced in Catalonia, Spain was 6,756 g $year^{-1}$, approximately 10% of that for PBDEs (57,757 g $year^{-1}$), and about 4 times that for HBCD (1,558 g $year^{-1}$) (Gorga et al., 2013), indicating the widespread environmental occurrence of DBDPE in the Spanish environment. Moreover, it is noticeable that concentrations of DBDPE exceeded that of BDE-209 in non-e-waste recycling areas of China (Zheng et al., 2011).

Table 1.11 Summary of concentrations of DBDPE in various environmental matrices (mean values in parentheses)

Matrix	Description	Concentration	Reference
Outdoor Air (pg m^{-3})	Five sites, Great Lakes region	1.2-5.2 (averaged over the years 2005-11)	Ma et al., 2013
	Pearl River Delta, China (2007)	402-3578	Shi et al., 2009
Indoor Air (pg m^{-3})	Electronics dismantling facility, Sweden	700 (n=1)	Kierkegaard et al., 2004
	Dismantlers, electronic recycling facility, Sweden	0.01-1.2 (0.06)	Pettersson-Julander et al., 2004
	Other workers, electronic recycling facility, Sweden	0.01-0.09 (0.04)	
	Unexposed, electronic recycling facility, Sweden	0.01-0.01 (0.01)	
Indoor Dust (ng m^{-3})	Homes, UK	n.d.-3400 (270)	Harrad et al., 2008a
	Offices, UK	n.d.-860 (170)	
	Cars, UK	n.d.-2900 (400)	
	Classrooms, West Midlands, UK (2007-8)	<20-2467 (293)	Ali et al., 2011a
	Homes, Antwerp, Belgium (2008)	55-2126 (303)	
	Offices, Antwerp, Belgium (2008)	170-1846 (789)	
	Floor and mattress dust, Rural and urban New Zealand	<5-1430	Ali et al., 2012
	Eastern Romania	median 170	Dirtu et al., 2012
	E-waste storage facilities, Thailand	43-8700 (1300)	Muenhor et al., 2010
	Main living area, greater Boston, MA area, US (2006)	<10-11070 (138)	Stapleton et al., 2008
	Bedroom, greater Boston, MA area, US (2006)	<10-3420 (153)	
	Home vacuum bag, greater Boston, MA area, US (2006)	<10-262 (39.4)	
	Various Thai e-waste facilities	380-44000 (8630) median 4650	Ali et al., 2011b
	Ground close to e-waste dismantling workshops, China (2006)	<2.5-139	Shi et al., 2009
	E-waste workshop, south China	171-7450 (3030)	Zheng et al., 2011
	Resident in e-waste recycling area, south China	399-5330 (1080)	
	Urban area, south China	100-46700 (2730)	
	Rural area, south China	104-733 (485)	
Water (ng L^{-1})	E-waste recycling site, south China (2006)	n.d.	Wu et al., 2010
Sediment (ng g^{-1} dw)	Western Scheldt, Netherlands	24 (n=1)	Kierkegaard et al., 2004
	Llobregat and Anoia River, Spain (2005-6)	4.8-24	Guerra et al., 2010
	River Arga, Nalón, and Besós, Spain (2012)	<80-435	Cristale et al., 2013
	Durban Bay and 13 rivers, South Africa (2011)	n.d.- 1840 (171) ng g^{-1} TOC	La Guardia et al., 2013
	Pearl River Delta, Southern China (2002/6)	38.8-364	Shi et al., 2009
	San Francisco Bay (2007)	<24	Klosterhaus et al., 2012
	E-waste recycling site, south China (2006)	Average 1796 ng g^{-1} ww (n=6)	Wu et al., 2010

Matrix	Description	Concentration	Reference
Sewage Sludge (ng g^{-1} dw)	Sewage treatment plants, Sweden	52; 32 (n=2)	Kierkegaard et al., 2004
	17 wastewater treatment plants, Catalonia, Spain (2009)	<12.1-257	Gorga et al., 2013
	Pearl River Delta, Southern China (2007)	266-1995	Shi et al., 2009
Soil (ng g^{-1} dw)	Farmland, Pearl River Delta, Southern China (2007)	17.6-35.8	Shi et al., 2009
	E-waste Processing area, China (2006)	<2.50-4.56	
Birds (ng g^{-1} lw)	Cormorant eggs, San Francisco Bay (2008)	Not reportable	Klosterhaus et al., 2012
	Muscle, Liver, Kidney, E-waste Processing area, China	<9.6-54.6	Shi et al., 2009
Panda (ng g^{-1} lw)	tissue, China	< 0.1-863	Hu et al., 2008
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Muscle and liver of juvenile sole, French coast (2007-9)	<n.d.-21.2 (pg g^{-1} ww)	Munschy et al., 2011
	White croaker, San Francisco Bay (2006)	Not reportable	Klosterhaus et al., 2012
	Shiner surfperch, San Francisco Bay (2006)	Not reportable	
	Seal blubber, adults, San Francisco Bay (2007/8)	Not reportable	
	Seal blubber, pups, San Francisco Bay (2007/8)	Not reportable	
	Fish muscle tissues and livers, e-waste processing area, China	< 3.8	Shi et al., 2009
	Fish, Lake Winnipeg, Canada	< 0.1-2.71	Law et al., 2006
Food (ng g^{-1} lw)	UK and Irish foods (meat, meat products, offal, fish, and fish products)	< 0.06	Fernandes et al., 2010
Human tissues (ng g^{-1} dw)	Hair, e-waste workshop, south China	5.92-365 (24.2)	Zheng et al., 2011
	Hair, resident in e-waste recycling area, south China	3.97-65.1 (17.7)	
	Hair, urban area, south China	6.05-88.7 (17.8)	
	Hair, rural area, south China	2.32-128 (9.57)	
Toys (ng g^{-1})	Toys purchased from South China	Median 5540	Chen et al., 2009

1.5.2.4 Environmental Fate of Other NBFRs

PBEB PBEB was used as an additive flame retardant in thermoset polyester resins (circuit boards, textiles, adhesives, wire and cable coatings, and polyurethanes) and thermoplastic resins during the 1970s and 1980s. Production in North America ranged between 45 and 450 tons in 1977, but its manufacture was discontinued at the end of the 1980s (USEPA, 1985 and 1988). In the EU, PBEB is listed as a limited production volume chemical (ESIS, 2010), with an estimated production volume in the EU of 10-1,000 tons in 2002 (OSPAR).

In North America, concentrations of PBEB in outdoor air were found to be decreasing with halving times of 5-10 years at most monitored sites over the period 2005-2011, but interestingly displayed an increasing trend at Eagle Harbor, the most remote site but with the highest PBEB levels (Ma et al., 2013).

The estimated accumulation of PBEB in sewage sludge produced in Catalonia, Spain was only 19 g $year^{-1}$, compared to 6,756 and 57,757 g $year^{-1}$ for DBDPE and PBDEs, respectively (Gorga et al., 2013); reflecting the limited production, use, and environmental release of PBEB in Spain.

TBBPA-DBPE TBBPA-DBPE is an additive BFR produced by the Albemarle Corporation, the Great Lakes Chemical Corporation, and some chemical corporations in China (USEPA 2007; Cai, 2008; ESIS, 2010), with major applications in plastic products such as: pipes, water barriers, kitchen hoods, and electronics (Ou and Li, 2006). The occurrence of TBBPA-DBPE in the environmental samples was first reported in 2009 in sediments from southern China (Shi et al., 2009).

TBECH TBECH was found to undergo degradation in both activated and digested sludge under aerobic conditions, and also in activated sludge under anaerobic conditions, with average half-lives (range) of 21 (19-23), 36 (32-42), and 23 (17-32) days, respectively (Nyholm et al., 2010). This suggests that TBECH is markedly less persistent in the environment compared to legacy BFRs like PBDEs.

Table 1.12 Summary of concentrations of PBEB in various environmental matrices (mean values in parentheses)

Matrix	Description	Concentration	Reference
Outdoor Air (pg m^{-3})	Potential source zones, city centre, Norway	<2	Arp et al., 2011
	Various sites, US	520 and 29 in gas and particle phase, respectively	Hoh et al., 2005
	Five sites, Great Lakes region	~0.1-3	Ma et al., 2013
Water (pg L^{-1})	Wastewater and seepage water, potential source zones, Norway	<120-940	Arp et al., 2011
	E-waste recycling site, south China (2006)	Average 60 (n=6)	Wu et al., 2010
Sediment (ng g^{-1} dw)	Sediment and seepage sediment, potential source zones, Norway	<0.01-0.028	Arp et al., 2011
	Llobregat and Anoia River, Spain (2005-6)	n.d.-9.6	Guerra et al., 2010
	River Arga, Nalón, and Besós, Spain (2012)	n.d.	Cristale et al., 2013
	San Francisco Bay (2007)	<0.03-0.1	Klosterhaus et al., 2012
	E-waste recycling site, south China (2006)	Average 132 ng g^{-1} ww	Wu et al., 2010
Sludge (ng g^{-1} dw)	Wastewater sludge, potential source zones, Norway	<0.25	Arp et al., 2011
	17 wastewater treatment plants, Catalonia, Spain (2009)	<0.58-2.33	Gorga et al., 2013
Birds (ng g^{-1} lw)	Cormorant egg, San Francisco Bay (2008)	<0.8	Klosterhaus et al., 2012
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Blubber of harbour porpoises, UK (2008)	<0.34-35 (ng g^{-1} ww)	Law et al., 2013
	White croaker, San Francisco Bay (2006)	<3.0	Klosterhaus et al., 2012
	Shiner surfperch, San Francisco Bay (2006)	<11.0	
	Seal blubber, adults, San Francisco Bay (2007/8)	0.07-0.5	
	Seal blubber, pups, San Francisco Bay (2007/8)	<0.08-0.2	

Table 1.13 Summary of concentrations of TBBPA-DBPE in various environmental matrices (mean values in parentheses)

Matrix	Description	Concentration	Reference
Outdoor Air (pg m^{-3})	Pearl River Delta, Southern China (2007)	131-1240	Shi et al., 2009
Indoor Dust (ng g^{-1})	Classrooms, West Midlands, UK (2007-8)	<20-9961 (729)	Ali et al., 2011a
	Homes, Antwerp, Belgium (2008)	<20-1286 (144)	
	Offices, Antwerp, Belgium (2008)	<20-2211 (608)	
	Various Thai e-waste facilities	<20-1770 (500) median 390	Ali et al., 2011b
	Ground close to the e-waste dismantling workshops, China (2006)	<1.5	Shi et al., 2009
Soil (ng g^{-1} dw)	Farmland, Pearl River Delta, Southern China (2007)	17.3-60.4	
	E-waste Processing area, China (2006)	<1.5	
Sediment (ng g^{-1} dw)	Pearl River Delta, Southern China (2002/6)	<1.5-2300	
Sewage Sludge (ng g^{-1})	Pearl River Delta, Southern China (2007)	238-8946	
Birds (ng g^{-1} lw)	Muscle, Liver, Kidney, E-waste Processing area, China	<2.3	
Aquatic invertebrates, fish and mammals (ng g^{-1} lw)	Fish muscle tissues and livers, e-waste processing area, China	< 2.3	

1.5.3 Human Exposure and Adverse Health Effects

In a study where personal air sampling strategies was used, atmospheric concentrations of BTBPE were significantly higher inside a dismantling hall than outside at an electronics recycling plant in Sweden (Pettersson-Julander et al., 2004), with occupational exposure implications for workers involved in e-waste dismantling. Moreover, while elevated BTBPE concentrations were detected from Chinese e-waste workers, compared to non-occupationally exposed residents from e-waste impacted area and an urban area, and control populations from non-e-waste treatment areas; DBDPE concentrations in hair of residents from e-waste impacted area and monitored urban area were similar (Zheng et al., 2011).

With respect to biomagnification capacity, while food web magnification was found for HBCD and PBDEs, trophic dilution of BTBPE through the food web was observed (Wu et al., 2010).

Overall, there is a very striking gap in knowledge on human exposure to NBFRs. Our currently limited knowledge suggests that human exposure to NBFRs occurs via similar pathways to other POPs with indoor applications like PBDEs and HBCDs, via inhalation, ingestion of indoor dust, and diet. Data on levels of NBFRs in human tissues is extremely scarce, with the only study of which we are aware being a report from South China. In this, concentrations of BTBPE and DBDPE in human hair were significantly correlated with that in paired indoor dust samples (Zheng et al., 2011), suggesting significant human exposure to these NBFRs in this population occurred via indoor dust ingestion. With respect to children, DBDPE was the dominant NBFR detected in children's toys (including hard/soft plastic toys, foam toys, and textile/stuffed toys) from China (Chen et al., 2009), suggesting toys could be a potential exposure pathway to NBFRs for children.

With respect to their toxicity, knowledge is extremely scarce. Concentrations of BTBPE and TBPH in indoor dust were found positively associated with total T3 levels in men aged 18-54, suggesting that exposure to BTBPE and TBPH via indoor dust may cause endocrine disruption in men (Johnson et al., 2013). Likewise, DBDPE causes concern due to its similar chemical structure to BDE-209. In contrast, current knowledge suggests BTBPE has low toxicity (Nomeir et al., 1993; Tomy et al., 2007).

1.6 Aims and Objectives

Current understanding of PCBs, PBDEs, HBCDs, and NBFRs reveals several research gaps with respect to our knowledge of their environmental presence, fate and behaviour, especially in the UK. In order to try and address these gaps, this project will:

a- Measure concentrations of several selected non-dioxin like-PCBs, as well as tri-through hexa-BDEs, and the three main HBCD diastereomers (α-, β-, and γ-HBCD) in water samples taken from 9 English freshwater lakes on 13 occasions between April 2008 and February 2012, and

b- Measure concentrations of the above POPs, plus BDE-183, BDE-209, and 32 NBFRs in radiometrically dated sediment cores (covering sedimentation from ~1950 to 2011/2) from 7 English lakes.

Based on these data, this thesis will address the following aspects of the environmental fate and behaviour of our target POPs. Specifically it will:

1- Identify and quantify the principal POPs in English lacustrine environments, and test the hypothesis that relative abundance is governed by their historical production and use, application mode, and physicochemical properties.

2- Elucidate the temporal trends in concentrations of POPs in water samples and dated sediment cores, and test the hypothesis that these temporal trends reflect changes in production and use of such POPs. This will incorporate evaluation of the environmental responses to bans and/or control measures applied to certain POPs, including increases in uses of some compounds as a result of restrictions on others. For example, signs of decline in concentrations of PCBs, PBDEs, and HBCDs, and indications of increasing concentrations of NBFRs in the UK.

3- Elucidate the spatial trends in concentrations of POPs in water samples and dated sediment cores across all sites, testing the hypothesis that such spatial variation exists and is influenced by factors such as: TSS content, population density, lake surface area, lake catchment area, and lake catchment ratio.

4- Enhance understanding of the fate and behaviour of our target POPs in lacustrine environments. This includes improving our comprehension of seasonal variations in their

concentrations in water and their partitioning between water and surficial and suspended sediment.

5- Facilitate estimation of the outdoor environmental burdens of our monitored POPs in the UK.

Chapter Ⅱ

Sampling & Analytical Methodology

2.1 Overview

For English lake water samples, the analytical methodology for determination of BFRs (PBDEs and HBCD) and PCBs in this thesis generally consisted of six major steps: sampling, filtration, drying, extraction, clean-up and instrumental analysis. For English sediment core samples, PCBs, PBDEs and HBCDs, and 32 NBFRs were targeted; the analysis of which involved seven steps: sampling, core sectioning, freeze-drying, dating, extraction, clean-up, and instrumental analysis. Sediment density, moisture content, and total organic carbon (TOC) was also determined. For the suspended sediment samples studied from the Niagara River, only HBCDs were targeted and analysed. The steps involved here were: sampling, freeze-drying, column clean-up, and instrumental analysis. In this chapter, each of the above procedures will be described in detail with full information given. Method validation, quality assurance and quality control measures employed in this study will be presented as well.

2.2 Sampling

2.2.1 English Lake Water Sampling

A map of the sampling locations is provided as Figure 2.1, with more details shown in Table 2.1. The 9 lakes in this study possess a variety of features: Slapton Ley is the largest natural lake in south-west England; although it is only separated from the sea by a narrow single bar, it is entirely freshwater; Edgbaston Pool is almost in the centre of Birmingham, the second biggest city in England; Crag Lough is in a rolling moorland area at the north-east end of England, with the lowest surrounding population density of all lakes in this study; while Wake Valley Pond is located in an ancient woodland 24 km north-east of central London, yet has the largest surrounding population density in this study. Moreover, 5 of our lakes are sites of Special Scientific Interest (SSSI), which are protected areas with conservation designation.

Sampling was conducted on 13 occasions from each of our 9 freshwater lakes throughout England; however one sample for THOP was missing due to drought on one sampling occasion, and one sample for analysis of PBDEs at THOP was lost in analysis, making 115 samples in total for PBDEs, and 116 samples for PCBs. HBCDs were not determined in the

first sample batch, making 107 samples in total for HBCDs. Initially, between April 2008 to July 2010, sampling frequency was quarterly, switching to biannually thereafter until the last sampling event in February 2012 (more details on sampling dates are supplied in Table 2.2). On each sampling occasion, a grab sample of 40 L of water was collected from 50 cm below the water surface in 2 × 20 L pre-cleaned high density polyethylene (HDPE) containers, at the profundal (deepest) point of each target location (except at WAKE where the deepest point was not suitable as a general sampling point due to the special shape of the lake bed). Caution was taken to minimise contamination at all levels of sampling and handling procedures. Samples were delivered to Birmingham directly after each sampling trip.

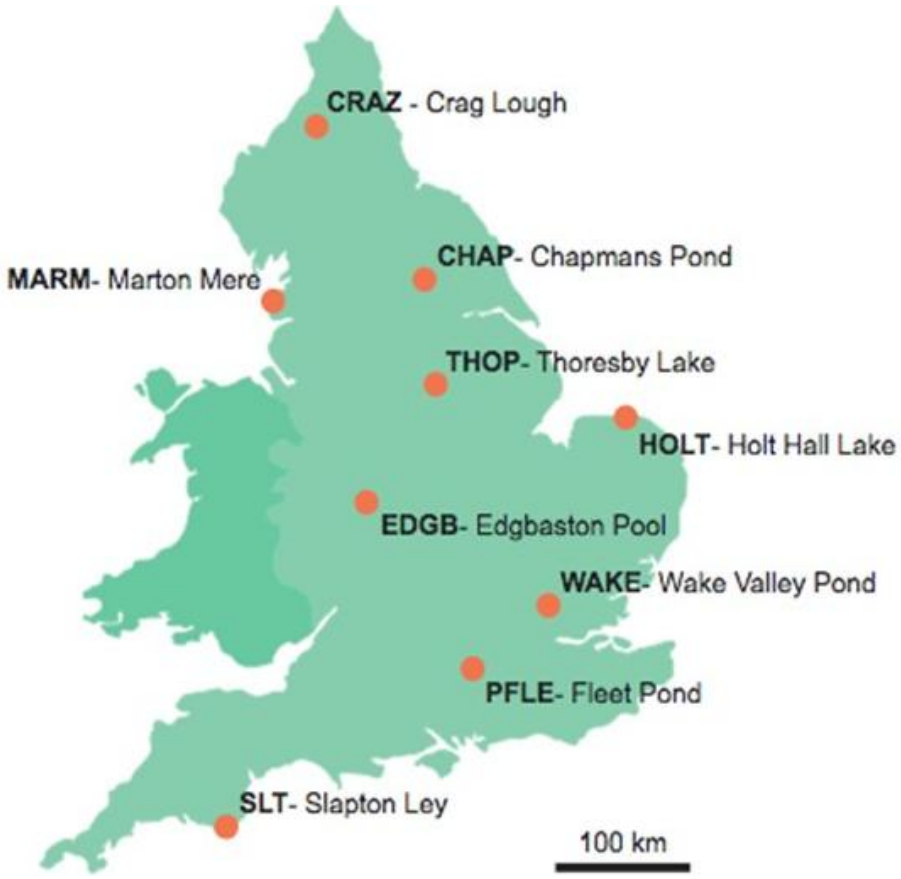


Figure 2.1 Sampling locations in this study

Table 2.1 Information on sampling locations

Site Name	Latitude	Longitude	Altitude (m)	Lake Area (ha)	Mean Depth (m)	Profundal Depth (m)	Population density (people km^{-2}) of local/unitary authority of lake site	Population density (people km^{-2}) of local/unitary authorities within 25km of site
Chapman's Pond (CHAP)	53.9344 °N	1.1201 °W	16	0.6	2.13	4.5	500-999	1000-2499
Crag Lough (CRAZ)	55.0058 °N	2.3672 °W	244	10.1	1	2	≤99	≤99
Edgbaston Pond (EDGB)	52.4546 °N	1.9209 °W	127	7.2	0.9	2.1	>2500	>2500
Holt Hall Lake (HOLT)	52.9154 °N	1.0873 °E	47	0.7	0.6	1	100-249	100-249
Marton Mere (MARM)	53.8093 °N	3.0004 °W	7	10.8	1.35	4.15	>2500	>2500
Fleet Pond (PFLE)	51.2890 °N	0.8257 °W	68	26.4	0.5	0.8	250-499	>2500
Slapton Ley (SLT)	50.2743 °N	3.6534 °W	3	65.9	-	2.5	≤99	1000-2499
Thoresby Lake (THOP)	53.2272 °N	1.0564 °W	37	30.4	1.4	3.1	100-249	1000-2499
Wake Valley Pond (WAKE)	51.6695 °N	0.0530 °E	96	1	1.7	3.7	250-499	>10000

Altitudes and areas from http://www.uklakes.net/

Population Density of England by local or unitary authority, 2007

Data from:http://www.statistics.gov.uk/default.asp

Table 2.2 Sampling dates in this study

	Apr-2008	Jul-2008	Nov-2008	Jan-2009	Apr-2009	Jul-2009	Oct-2009	Jan-2010	Apr-2010	Jul-2010	Feb-2011	Jul-2011	Feb-2012
CHAP	30/04/08	12/08/08	16/11/08	21/01/09	22/04/09	11/07/09	18/10/09	31/01/10	16/04/10	15/07/10	02/02/11	20/07/11	13/02/12
CRAZ	01/05/08	18/08/08	15/11/08	22/01/09	23/04/09	08/07/09	18/10/09	31/01/10	16/04/10	16/07/10	03/02/11	26/07/11	12/02/12
EDGB	05/05/08	17/08/08	13/11/08	25/01/09	28/04/09	16/07/09	14/10/09	03/02/10	19/04/10	21/07/10	07/02/11	21/07/11	15/02/12
HOLT	29/04/08	02/08/08	11/11/08	20/01/09	22/04/09	15/07/09	13/10/09	30/01/10	15/04/10	14/07/10	02/02/11	24/07/11	14/02/12
MARM	02/05/08	15/08/08	14/11/08	23/01/09	24/04/09	10/07/09	17/10/09	01/02/10	17/04/10	17/07/10	04/02/11	27/07/11	12/02/12
PFLE	04/05/08	31/07/08	06/11/08	24/01/09	25/04/09	14/07/09	16/10/09	03/02/10	18/04/10	19/07/10	06/02/11	23/07/11	11/02/12
SLT	03/05/08	30/07/08	07/11/08	24/01/09	25/04/09	12/07/09	15/10/09	02/02/10	18/04/10	20/07/10	05/02/11	22/07/11	11/02/12
THOP	28/04/08	03/08/08	12/11/08	21/01/09	27/04/09	07/07/09	13/10/09	04/02/10	-	22/07/10	07/02/11	19/07/11	15/02/12
WAKE	28/04/08	01/08/08	10/11/08	19/01/09	21/04/09	06/07/09	12/10/09	29/01/10	14/04/10	13/07/10	01/02/11	25/07/11	14/02/12

2.2.2 Lake Sediment Core Sampling & Sectioning

Sediment core sampling was conducted from a boat at six of the nine monitored lakes in July 2011 with MARM sampled in March 2012, making seven sediment cores in total using a polycarbonate tube with an inner diameter of 71 mm. After collection from the deepest area (generally the central lake point), sediment cores were kept vertical and still for at least 1 hour to stabilise. Sediment cores were sectioned with an extruding interval of 1 cm on site, with an O-ring of 1 cm height with the same i.d. as the polycarbonate tube, and a stainless steel cutter. Each segment was divided into two during the sectioning procedure: two thirds of each slice was collected into pre-cleaned 100 mL glass jars - distilled water (DDW) and then dichloromethane (DCM) and hexane rinsed, for POPs analysis; with the remaining one third kept in self-sealed bags, one portion was used for determination of sediment density, moisture content and TOC content, with the rest used for radiometric dating.

After freeze-drying, each core slice was homogenised and combined to provide a number of sediment samples that radiometric dating result indicated covered around five years of sedimented material.

2.2.3 Niagara River Suspended Sediment Sampling

Suspended sediment sampling was conducted in March, April/May, Jun, July, and August between 1980 and 2012 at Niagara-on-the-Lake sampling station, which is at the mouth of the Niagara River in Lake Ontario (around 1 km upstream of Lake Ontario) at the Canadian side (see Figure 2.2).

Bulk water was sampled for approximately 24 hours (about 50 m away from the river bank, 7 m above the river bed, and 6 m below the surface), using sampling equipment consisting of an intake line, several pumps, a suspended solids collector (Westphalia centrifuge) and a Goulden large sample extractor. Water was pumped through a coarse basket filter and then a centrifuge where suspended sediment was separated from the bulk water sample. Suspended sediment was freeze dried and archived until analysis.

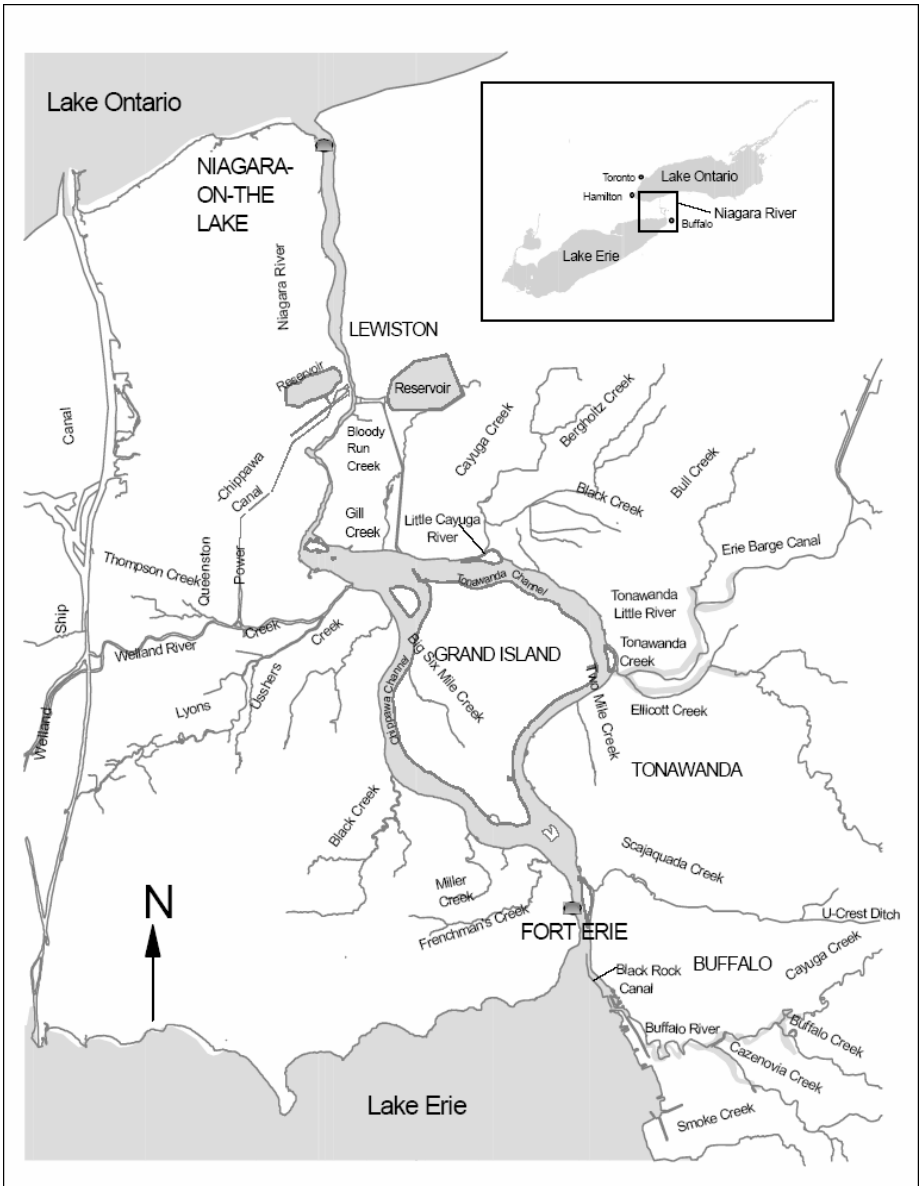


Figure 2.2 Sampling location: Niagara-on-the-Lake station

2.3 Sample Preparation and Extraction

2.3.1 English Lake Water

2.3.1.1 Water Filtration

Water samples were filtered via gravity through a glass fibre filter (GFF, 12.5 cm diameter, 1 μm pore size, Whatman, U.K.) to collect particulate matter, followed by two pre-cleaned polyurethane foam (PUF) plugs (8 cm diameter, 4 cm height, 0.03 g cm^{-3} each, PACS, Leicester, U.K.). The filters were baked in the furnace at 500 ℃and then DCM rinsed before

use. The PUF plugs were washed with double-distilled water (DDW), left to dry and Soxhlet extracted with DCM for 8 hours before use. Following filtration, the GFF and 2 PUF plugs were covered with DCM rinsed aluminium foil, and left on the bench over night to air-dry.

2.3.1.2 Measurement of Total Suspended Solids (TSS)

The TSS content of samples (40 L each) taken from all sites in February 2011 were chosen randomly and determined gravimetrically after filtration, ranging from 0.32 (at HOLT) to 46 mg L^{-1} (at PFLE). In addition, TSS contents were determined in all samples using smaller aliquots (around 1 L for each sample) by our collaborators in University College London (UCL). Both data are listed in Table 2.3.

2.3.1.3 Water Sample Extraction

The GFF and the two PUF plugs for each sample were combined as one sample and spiked with appropriate quantities of the following internal standards: $^{13}C_{12}$-labelled BDE-28, -47, -99, and -153 (Wellington Laboratories, Canada); PCBs 34, 62, 119, 131, and 173 (Dr. Ehrenstorfer GmbH, Germany); and $^{13}C_{12}$-labelled α-, β-, and γ-HBCD (Wellington Laboratories, Canada), and then Soxhlet extracted with DCM for 8 hours as described elsewhere (Harrad et al., 2009). For those samples taken in summer 2008, the filters and PUFs were analysed separately to provide information on the operationally defined particulate phase and dissolved phase.

Table 2.3 TSS concentrations (mg L^{-1}) of water samples, with measurements made using 40 L water in February 2011 presented in parentheses

Location / Date	CHAP	CRAZ	EDGB	HOLTU	MARM	PFLE	SLT	THOP	WAKE
2008/04	8.5	2.8	0.8	0.6	1.2	32.2	2.2	20.0	5.3
2008/07	10.5	3.3	4.1	0.6	3.9	51.0	8.3	1.2	11.2
2008/11	6.8	7.0	6.6	1.7	3.0	21.3	0.8	17.3	9.7
2009/01	3.6	3.5	4.3	2.2	2.4	21.8	7.4	13.9	4.4
2009/04	8.0	0.9	9.2	1.4	2.7	48.4	1.8	9.1	3.8
2009/07	13.6	3.7	2.0	1.7	1.4	51.4	3.6	1.1	2.6
2009/10	14.0	1.4	1.4	2.1	1.6	20.2	1.5	2.5	3.5
2010/01	5.6	1.3	5.5	1.8	5.3	18.9	2.9	5.1	2.9
2010/04	13.5	2.0	2.8	1.2	2.1	38.8	4.2		4.8
2010/07	10.2	12.9	3.2	1.5	6.0	60.0	28.9	2.1	3.5
2011/02	9.1 (2.3)	13.4 (11.0)	7.8 (3.4)	1.1 (0.32)	8.6 (5.7)	50.7 (45.7)	6.1 (3.1)	19.1 (16.1)	4.7 (3.5)
2011/07	13.6	4.7	3.2	2.6	1.3	39.2	19.0	1.5	4.7
2012/02	1.9	2.5	13.8	1.9	1.5	8.7	3.0	10.7	4.7

2.3.2 English Lake Sediment Core Samples

2.3.2.1 Sediment Density, Moisture Content & Total Organic Carbon (TOC) Sediment density was determined using a copper cube with 2 cm^3 capacity. The moisture content was by determining the mass lost by drying at 100 ˚C overnight. Dry sediment mass (DSM) of each sediment slice used for input flux estimation was calculated using equation 2.1:

DSM = (sediment density) * (sediment volume) * [(dry weight)/ (wet weight)] (2.1)

Dry sediment masses used for POPs analysis were 1.7-11.2 (average=6.2) g, depending on the amount of dry sediment material available for each individual core slice. Organic matter content was determined by loss-on-ignition (LOI) at 550 ˚C, and was considered to approximate to TOC. Defined thus, the TOC contents in sediment core slices ranged from 0.5 to 3.3 g, averaged at 1.7 g across all samples.

2.3.2.2 Radiometric Dating of Sediment Cores (^{210}Pb Dating)

Freeze-dried sediment samples were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay in the Bloomsbury Environmental Isotope Facility (BEIF) at UCL, using an ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector. ^{210}Pb was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV gamma rays emitted by its daughter isotope ^{214}Pb, following 3 weeks storage in sealed containers to allow radioactive equilibration. Caesium-137 and ^{241}Am were measured by their emissions at 662 keV and 59.5 keV (Appleby et al., 1986). The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy gamma rays within the sample (Appleby et al., 1992). The validation of ^{210}Pb dates calculated using the CRS model (Appleby, 2001) were double-checked via comparison with that recorded by ^{137}Cs and ^{241}Am. The chronologies and sedimentation rates were calculated using ^{210}Pb data. Corrections were made for the effect of self absorption of low energy gamma rays within the sample (Appleby et al., 1992). Dating results are shown in Figure 2.3.

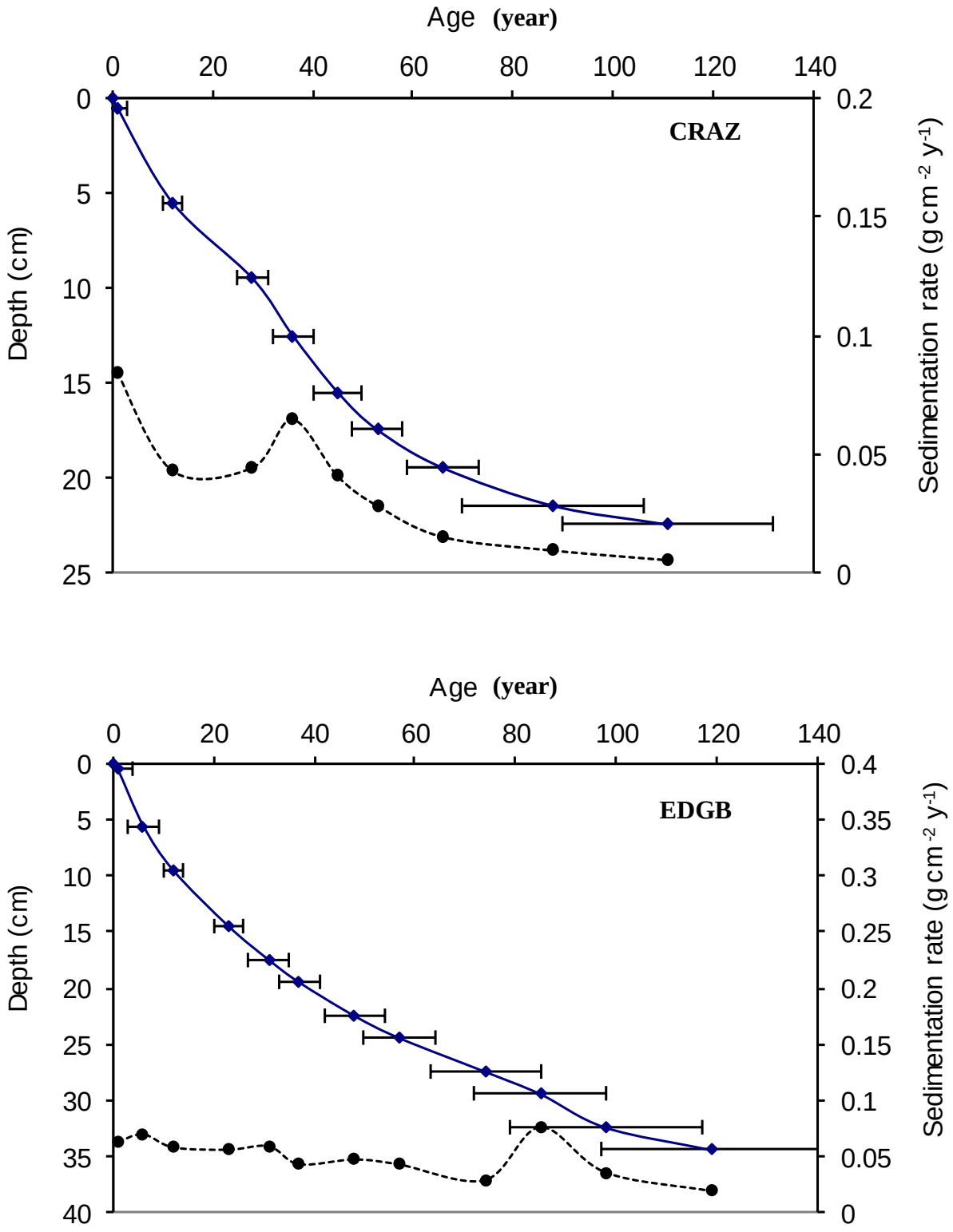


Figure 2.3 Part 1: Radiometric chronology for sediment cores from CRAZ and EDGB, showing sedimentation age (solid line; blue) and sedimentation rate (dashed line; black)

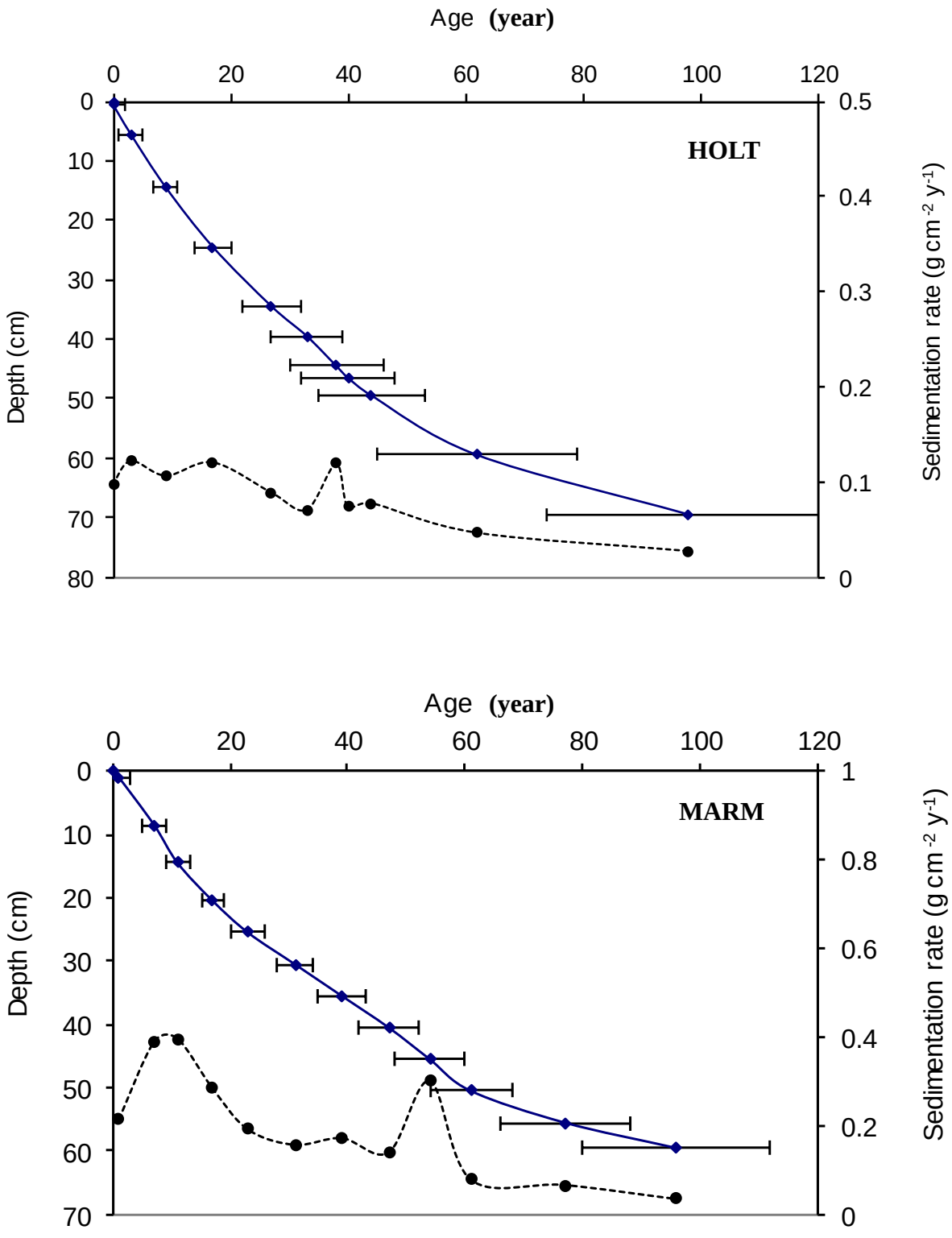


Figure 2.3 Part 2: Radiometric chronology for sediment cores from HOLT and MARM, showing sedimentation age (solid line; blue) and sedimentation rate (dashed line; black)

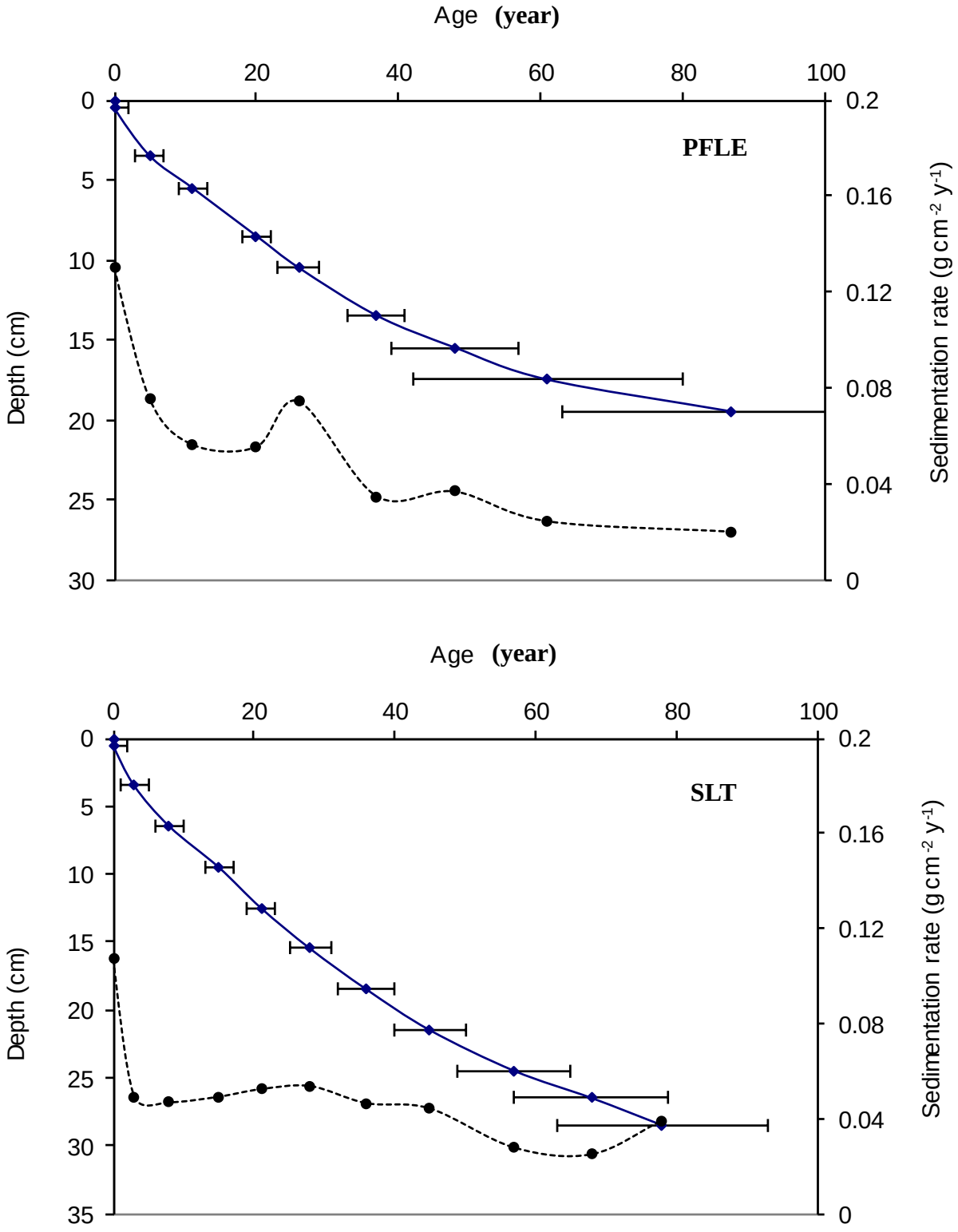


Figure 2.3 Part 3: Radiometric chronology for sediment cores from PFLE and SLT, showing sedimentation age (solid line; blue) and sedimentation rate (dashed line; black)

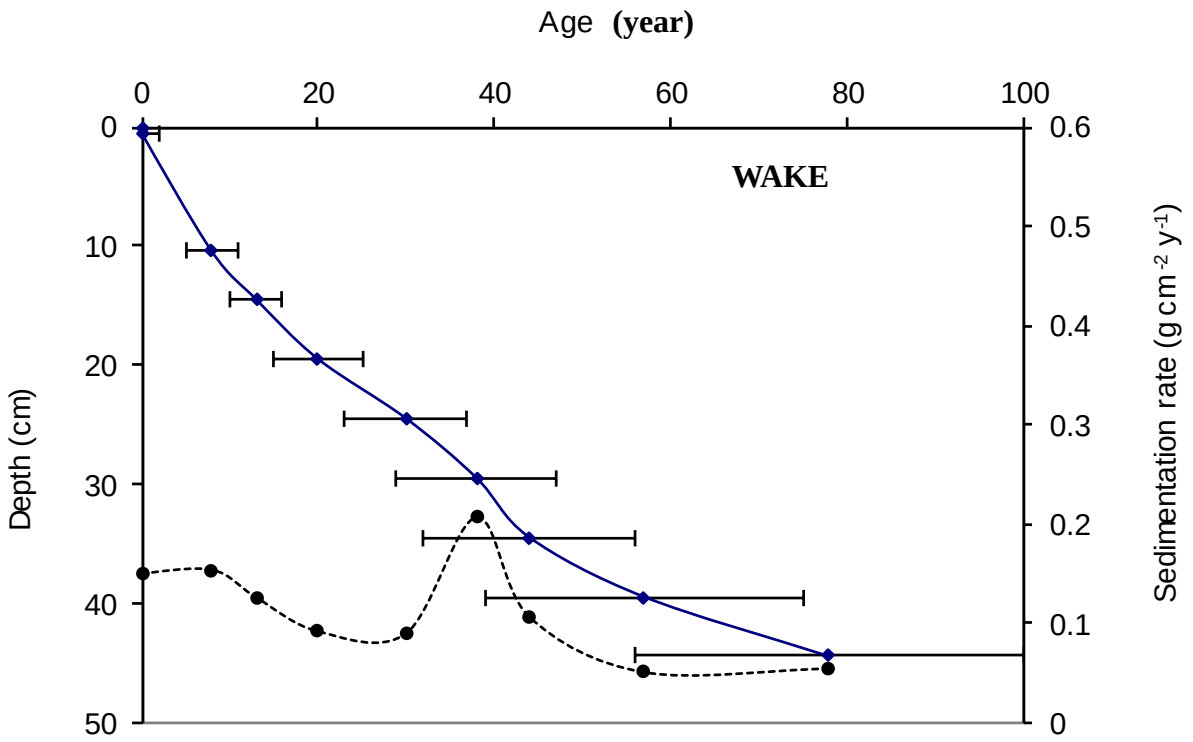


Figure 2.3 Part 4: Radiometric chronology for sediment cores from WAKE, showing sedimentation age (solid line; blue) and sedimentation rate (dashed line; black)

2.3.2.3 Sediment Core Sample Extraction

The analysis method used here for determination of a selection of NBFRs and PBDEs was developed by our collaborators at the Centre for Environment, Fisheries & Aquaculture Science (Cefas), England.

Following removal from the freezer for analysis, sediment samples were left to reach room temperature for approximately 30 minutes. Each sample was then extracted using a Speed Extractor (E-916 mode, BÜCHI, Switzerland). Hexane and acetone pre-cleaned hydromatrix and 5 g of sodium sulfate were first loaded into pre-cleaned 40 mL extraction cells. Sediment samples were then accurately transferred into the cells and spiked with ^{13}C-labelled BDE-3, BDE-28, BDE-47, BDE-99, BDE-153, and BDE-209 (Wellington Laboratories, Canada), PCBs 34, 62, 119, 131, and 173 (Dr. Ehrenstorfer GmbH, Germany), and $^{13}C_{12}$-labelled α-, β-, and γ-HBCDs (Wellington Laboratories, Canada); details on NBFRs standards are supplied in Table 2.4 (Law et al., 2013). Sediment materials were then topped with hydromatrix to fill remaining void space in the cells. The speed extractor cells were extracted with hexane:

acetone (1:1, v/v) at 100 ˚C and 120 bar for 3 cycles, 5 min per cycle. The purge time and flush time were both 1 min. Sample extracts were collected in 240 mL glass collection vials containing 5 g pre-cleaned copper wire (for sulfur removal) and stored overnight.

2.3.3 Niagara River Suspended Sediment Samples

Filtered suspended sediment samples were freeze-dried. A proportion of each sample was weighed accurately, and Soxhlet extracted with toluene for approximately 12-16 hours. As in this study, the samples were provided as archived sample extracts that had been initially prepared with the intention of determining certain POPs, e.g., PBDEs (data has been partially published by Marvin et al., 2007); no isotopically labelled HBCDs were present, and thus quantification of HBCDs was conducted using the $^{13}C_{12}$-labelled BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209 standards (Wellington Laboratories, Canada) added prior to extraction.

Table 2.4 Information on precursor and product ions, instrumental limit of detection (LOD), and recoveries of monitored NBFRs

Abbreviation	Compound name	Precursor ions (m/z)	Product ions (m/z)	LOD (pg injection^{-1})	Recovery (%)
ATE (TBP-AE)	2,4,6-tribromophenol allyl ether	290.9 + 328.8	210.0 + 300.8	0.4	60-89
DiBTrCcH (PBCCd)	Dibromotrichlorocyclohexane	263.9	148.0 + 183.0	0.7	81-91
TeBDiCcH (PBCCc)	Tetrabromodichlorocyclohexane	263.9	148.0 + 183.0	0.5	70-77
α-DBE-DBCH	α-1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane	187.0 + 266.9	107.1 + 187.0	1.0	70-87
β-DBE-DBCH	β-1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane	187.0 + 266.9	107.1 + 187.0	1.0	80-98
δ-DBE-DBCH	δ-1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane	187.0 + 266.9	107.1 + 187.0	2.6	
γ-DBE-DBCH	γ-1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane	187.0 + 266.9	107.1 + 187.0	2.6	
BATE	2-bromoallyl 2,4,6-tribromophenyl ether	329.8	300.8 + 249.6	1.0	72-83
pTBX	2,3,5,6,-tetrabromo-p-xylene	421.7 + 340.8	340.8 + 261.9	0.4	80-85
TrBTrCcH (PBCCb)	Tribromotrichlorocyclohexane	306.8	226.9 + 148.0	2.1	57-61
β-TBCO	β-1,2,5,6-tetrabromocyclooctane	187.0 + 266.9	107.1 + 187.0	1.0	88-131
TBCT (TBoCT)	Tetrabromo-o-chlorotoluene	360.7 + 441.7	280.8 + 360.7	0.4	72-83
α-TBCO	α-1,2,5,6-tetrabromo cyclooctane	187.0 + 266.9	107.1 + 187.0	5.2	
PBCC (PeBCCH)	1,2,3,4,5-pentabromo-6-chlorocyclohexane	351.8 + 432.7	272.9 + 351.8	4.2	48-59
PBT	2,3,4,5,6-pentabromotoluene	327.8 + 487.6	246.9 + 406.7	0.4	10-20
PBP	Pentabromophenol	485.6 + 297.8	300.9 + 220.8	-	-
PBEB	Pentabromoethylbenzene	259.9 + 484.6	180.0 + 406.7	1.0	84-96
DPTE (TBP-DBPE)	2,3-dibromopropyl-2,4,6-tribromophenyl ether	329.8	249.8 + 302.	4.1	88-90
PBBB	Pentabromobenzylbromide	326.8 + 484.6	247.9 + 406.7	110	6.7-11
HBB	Hexabromobenzene	391.7 + 469.8	231.8 + 391.7	0.4	76-83
PBB-Acr (PBBA)	2,3,4,5,6-pentabromobenzylacrylate	406.7 + 484.6	326.8 + 406.7	7.0	11-37
HCDBCO (DBHCTD)	Hexachlorocyclopentadienyldibromocyclooctane	265.0 + 275.0	229.0 + 238.0	1.0	73-78
TBB (EH-TBB)	2-ethylhexyl-2,3,4,5-tetrabromobenzoate	392.7 + 436.7	312.0 + 420.7	2.0	22-37
diMeTBBPA	Dimethyl tetrabromobisphenol A	554.8	290.8 + 475.8	1.0	78-117
BB153	2,2′,4,4′,5,5′-hexabromobiphenyl	548.6 + 627.5	467.7 + 546.6	0.4	54-74
BTBPE	1,2-bis (2,4,6-tribromophenoxy) ethane	355.8	197.0 + 277.9	4.0	62-77
TBPH (BEH-TEBP)	Bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate	384.2 + 464.7	340.8 + 384.2	54	60-105
s-DP (s-DDC-CO)	syn-Dechlorane Plus	271.8 + 296.6	226.7 + 237.7	0.4	79-83
a-DP (a-DDC-CO)	anti-Dechlorane Plus	271.8 + 296.6	226.7 + 237.7	0.4	74-117

Abbreviation	Compound name	Precursor ions (m/z)	Product ions (m/z)	LOD (pg injection^{-1})	Recovery (%)
OBTMPI (OBIND)	Octabromotrimethylphenyl indane	297.7 + 451.8	219.8 + 372.9	15	70-110
TBBPA-DBPE	TBBPA-dibromopropyl ether	463+382.7	383+301.8	51	72-114
DBDPE	Decabromo diphenyl ethane	485.6+405.7	405.7+326.8	12	-
$^{13}C_6$-HBB	Hexabromo[$^{13}C_6$]benzene	397.7 + 477.6	316.8 + 397.7	N/A (IS)	N/A (IS)
$^{13}C_6$-PBP	Pentabromo[$^{13}C_6$]phenol	306.8 + 495.7	224.8 + 335.8	N/A (IS)	N/A (IS)
$^{13}C_6$-BTBPE	1,2-bis (2,4,6-tribromo[$^{13}C_6$]phenoxy) ethane	363.8	255.9 + 283.9	N/A (IS)	N/A (IS)

2.4 Clean Up

2.4.1 Clean Up of English Lake Water Samples

Following extraction, crude extracts were concentrated and then separated into two equal portions. The half used for analysis of PBDEs, and PCBs was subjected to Florisil column (1 g) clean up. Analytes were eluted first with 15 mL hexane and then 15 mL DCM. The hexane and DCM eluates were then extracted with dimethyl sulfoxide (DMSO) (3 x 10 mL). The DMSO extracts were combined, diluted with 35 mL deionized DDW and extracted sequentially with hexane (3 x 30 mL). The combined hexane extracts were then evaporated to incipient dryness under a stream of nitrogen (Turbovap). Final sample extracts were diluted in 50 µL hexane containing $^{13}C_{12}$BDE-100, PCB 19 and PCB 129 as recovery determination standards (RDS).

The remaining half of the crude extract was cleaned up through an 8 g acidified silica gel column topped with Na_2SO_4 as described previously (Harrad et al., 2009). HBCDs were eluted with 30 mL DCM/hexane (1:1, v:v). Eluates were then concentrated to near dryness using a Turbovap, and final sample extracts were diluted in 50 µL hexane containing d_{18}-γ-HBCD as a recovery determination standard RDS.

2.4.2 Clean Up of English Lake Sediment Core Samples

Sediment core samples in this study were cleaned up with a more extensive procedure due to its complicated matrix. Briefly, three major clean up techniques were conducted for removal of sulfur, and lipids, etc, see below for details.

2.4.2.1 Hydrophilic PTFE Filter Filtration

Sample extracts were transferred into Syncore tubes and concentrated to around 1 mL in a batch size of 12 with Syncore Polyvap Evaporator System, combined with a cooling system (BÜCHI). Syncore tubes were heated to 40 ℃ to enhance solvent evaporation speed, while the Syncore tube tips were kept at 0 ℃ for final volume control. The Syncore tube rack shaking speed was 230 rds per min. System pressure was decreased gradually starting from 400 psi then held at 150 psi. Sample extracts were then transferred to 10 mL centrifuge tubes and solvent exchanged to approximately 0.5 mL cyclohexane: ethyl acetate (1:1, v/v).

Samples extracts in cyclohexane:ethyl acetate (1:1, v/v) were filtered using a *Samplicity* Sample Filtration System (High Throughput) with a 0.20 µm hydrophilic PTFE filter (Millex

Samplicity Filters, Millipore Ireland Ltd). Eluates were collected in amber Agilent injection vials and concentrated to around 1.3 mL.

2.4.2.2 GPC Clean Up of Sediment Core Samples

Samples were further cleaned up using a gel permeation chromatography system (GPC, Series 1100 HPLC system controlled by ChemStation software, Agilent technology). This comprised a sample rack, quaternary HPLC pump, vacuum degasser, auto-sampler (2-900 µL injection volume), UV detector (set at 254 nm), and fraction collector with 50 mL capacity glass vessels (30 mm x 100 mm). Two GPC columns (19 mm x 150 mm x 15 µm, and 19 mm x 300 mm x 15 µm, styrene/DVB polymeric material, Envirogel^{TM}, Waters, USA) combined with a 4.6 mm x 30 mm x 15 µm guard column (styrene/DVB polymeric material, Envirogel^{TM}, Waters, USA) were used. Injection volume was 900 µL, and the mobile phase was composed of cyclohexane: ethyl acetate (1:1, v/v) at 0.5 mL min^{-1}. See below for description of estimation of GPC eluate collecting time, GPC calibration and sample clean up.

2.4.2.2.1 Estimation of GPC Fraction Collecting Time

A GPC calibration standard solution containing 125 g L^{-1} corn oil, 5 g L^{-1} Bis(2-ethylhexyl)-phthalate (BEHP), 0.5 g L^{-1} methoxychlor, 0.1 g L^{-1} perylene, and 0.4 g L^{-1} sulfur in cyclohexane: ethyl acetate (1:1, v/v) was employed.

A mixture of the above GPC calibration standard solution and halogenated compounds including target NBFRs and BDE congeners were injected. Figure 2.4 shows the separation of GPC calibration standard solution. Fractions eluted between 10 to 35 min were collected with a batch of GPC collecting tubes in series. Between 10 to 25 min, fractions were collected every 0.5 min (2.5 mL), switching to each 2 min (10 mL) thereafter. Fractions were concentrated and analysed via GC-MS/MS to estimate retention times of target compounds. The start and end points for collection of fractions were obtained using Equation 2.2 and 2.3:

Fraction collection start time (min) = 0.14 * corn oil + 0.86 * BEHP (2.2)

Fraction collection end time (min) = 0.31 * methoxychlor + 0.69 * perylene (2.3)

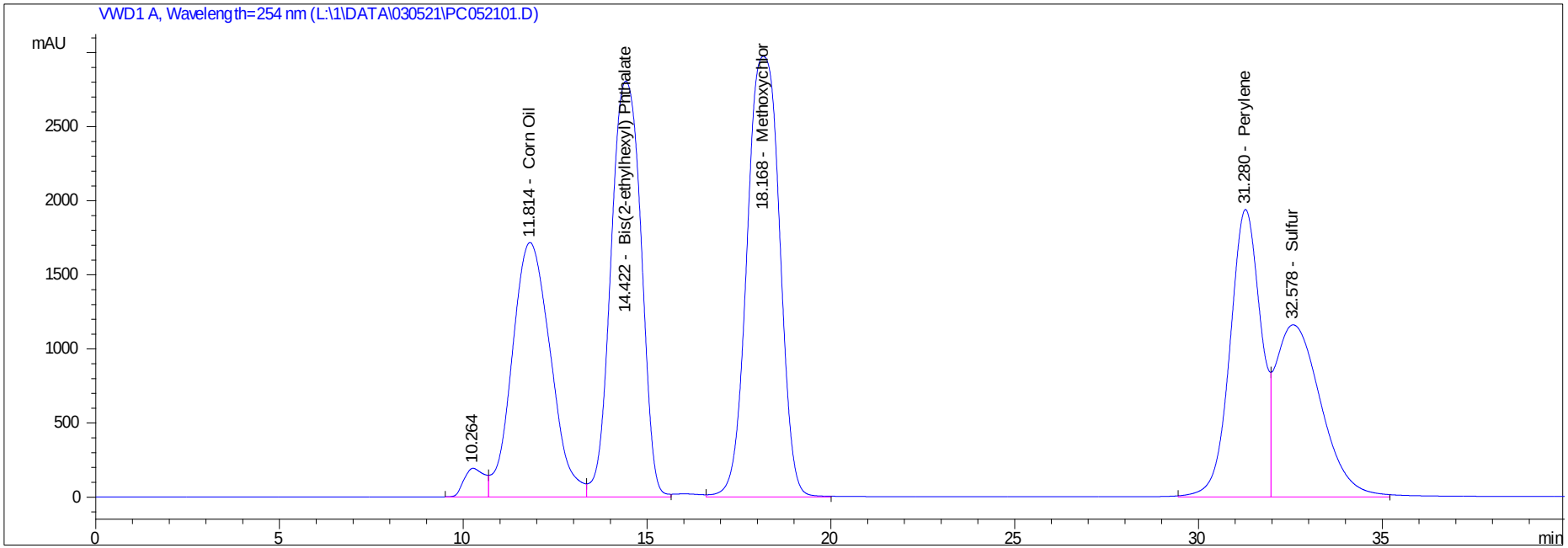


Figure 2.4 Typical separation of GPC calibration standard solution

2.4.2.2.2 GPC Calibration & Clean Up

Calibration of GPC system was performed at the beginning of a sample batch to check the retention times, and the start and end of fraction collection times were adjusted accordingly if there were changes in retention times. Instrument status and method accuracy were double checked by injecting the calibration standard after each sample batch. The GPC system showed good performance and stabilities during the analysis period.

For sediment samples, GPC fractions of around 60 mL (5 mL x ~ 14 min) were collected in 2 x 50 mL GPC collection tubes and then combined and concentrated using the Syncore system to around 1 mL, and solvent exchanged to around 1 mL *iso*-octane.

2.4.2.2.3 Florisil Column Clean Up

Samples were further cleaned up with Teflon-coated SPE tubes containing 8 g hexane pre-cleaned Florisil topped with 5 g sodium sulfate. Columns were conditioned with 50 mL hexane, and target compounds subsequently eluted with 55 mL hexane and 40 mL DCM. Sample eluates were collected in Syncore tubes and concentrated to around 200 µL, before solvent exchange to 50 µL nonane containing CB 200 as a recovery determination standard.

2.4.3 Clean Up of Niagara River Suspended Sediment Samples

Concentrated suspended sediment extracts were reconstituted with 5 mL hexane, and then cleaned up with acid/base/silver nitrate silica columns. HBCDs were eluted with 100 mL hexane followed by 80 mL mixture of DCM/hexane (1:1, *v:v*). Eluates were concentrated to dryness and reconstituted in 50 uL methanol containing $^{13}C_{12}$-labelled α-, β-, and γ-HBCD.

2.5 Instrumental Analysis

2.5.1 Analysis of PCBs & Tri to Hexa-BDEs on GC-MS

Tri- to hexa-BDEs, and PCBs were analysed via an Agilent 6850-5975 GC-MS operated in positive electron ionisation mode (EI^+) for both English lake water and sediment core samples, and ions were monitored in selective ion monitoring (SIM) mode. See the following sections for details.

2.5.1.1 Analysis of PCBs

For the separation of PCBs (CB 28, 52, 101, 118, 153, 138 and 180 were targeted), the oven program was 140 ˚C for 2 mins, ramped to 215 ˚C at 5 ˚C min^{-1} and held for 5 mins, then 5 ˚C

min^{-1} to 280 ˚C and finally 4 ˚C min^{-1} to 290 ˚C and held for 13 mins. Ions monitored were: m/z 255.95, 257.95, 289.95, 291.95, 325.90, 327.90, 359.90, 361.90, 393.85 and 395.85.

2.5.1.2 Analysis of Tri- to Hexa-BDEs

The analytical method employed for tri to hexa-BDEs is reported elsewhere (Harrad and Hunter, 2006). Briefly, 1 µL sample was injected with an auto-injector in splitless mode at 280˚C. PBDEs (BDEs- 17, -28, -49, -47, -66, -100, -99, -85, -154, and -153 were targeted) were separated on a VF-5 ms capillary column (30 m x 0.25 mm x 0.25 µm). The initial column temperature was 140 ˚C held for 2 mins, ramped to 200 ˚C at 5 ˚C min^{-1}, then 300 ˚C at 2 ˚C min^{-1} held for 5 mins, and 2 ˚C min^{-1} to 310 ˚C. Ions monitored were: m/z 403.8, 405.8, 415.8, 417.8, 483.8, 485.8, 495.8, and 497.8 for native and $^{13}C_{12}$-internal standards.

2.5.2 Analysis of BDE-183, BDE-209 via LC-APPI-MS/MS

Analysis of PBDEs using LC-APPI-MS/MS system has been published previously by Abdallah et al. (2009). The above analytical method was further modified by a colleague Cassandra Rauert, and adopted here in this study. Chromatographic separation of BDE-183, and BDE-209 in English lake sediment core samples was conducted via a C_{18} reversed phase analytical column (250 mm x 4.6 mm i.d., 3 µm particle size). The HPLC system was interfaced with a negative ionisation atmospheric pressure photo ionisation source (APPI). Injection volume was 10 uL. The mobile phase program started with 15% mobile phase A (methanol/water, 1:1, *v:v*) and 85% mobile phase B (20% toluene in methanol) at a constant total flow rate of 0.4 mL min^{-1}, and then programmed to 100% mobile phase B in 15 min, hold for 15 min, then a prompt drop to 85% mobile phase B in 0.01 min, and hold for 5 min. The optimised APPI source conditions and the major MS/MS parameters are listed in Table 2.5. BDE 183 and BDE 209 were monitored in MRM mode based on the ion transitions of m/z 658.6/78.6, and 486.6/78.8, respectively.

Table 2.5 Optimised APPI source conditions and MS/MS parameters

Parameter	Value
Curtain Gas	25.0 (a.u.)*
Collision Gas (CAD)	11 (˚C)
IonSpray Voltage (IS)	-1250.0 (V)
APPI Temperature	400 (˚C)
Probe nebulizer Gas (Ion Source Gas 1)	60 (Psi)
Auxillary Gas (Ion Source Gas 2)	55 (psi)
Declustering Potential (DP)	-5.0 (V)
Focusing Potential (FP)	-250.0 (V)
Entrance Potential (EP)	-12.0 (V)
Collision Energy (CE)	-75.0 (eV)
Collision Cell Exit Potential (CXP)	-8.0 (V)

*a.u. - arbitrary units

2.5.3 Analysis of HBCDs via LC-ESI-MS/MS

Diastereomer-specific analysis of HBCD is impossible using GC/MS techniques due to the thermal degradation, rearrangement, and isomeric inter-conversion of HBCDs at elevated temperatures (Budakowski and Tomy, 2003). LC-MS and LC-MS/MS techniques are therefore widely adopted for HBCD analysis.

2.5.3.1 English Lake Water and Sediment Samples

With respect to the instrumental analysis of HBCDs in English lake water and sediment cores, a method reported previously (Harrad et al., 2009) was used with some changes in mobile phase. Target compounds were analysed with a dual pump Shimadzu LC-20AB Prominence liquid chromatography equipped with a Sciex API 2000 triple quadropole mass spectrometer operated in electrospray negative ionisation mode (ESI^-). A SIL-20A auto-sampler and a DGU-20A3 vacuum degasser were used. Separation of α-, β-, and γ-HBCDs was achieved on a Varian Pursuit XRS3 C18 reversed phase analytical column (150 mm × 2 mm i.d., 3 μm particle size). The following mobile phase program was applied: (a) 1:1 methanol/water and (b) methanol at a flow rate of 180 μL min^{-1}; solvent (b) was 50% (v:v) in the initial mobile phase and then increased linearly to 100% over 4 min, held for 5 min and then decreased linearly to 88% over 1 min, followed by a quick drop to 50%, and held for 1 min. Post-elution of target compounds, the column was flushed thus: solvent (b) was increased gradually to 100% over 1 min, held for 6 min, finishing with 50% (b) for 4 min. The three HBCD diastereomers

were baseline separated with retention times of 9.0, 10.6, and 11.2 for α-, β-, and γ-HBCDs, respectively. MS/MS detection operated in the MRM mode was used for quantitative determination based on *m*/*z* 640.6/79, *m*/*z* 652.4/79, and *m*/*z* 657.7/79 for the native, ^{13}C-labelled, and d_{18}-labelled HBCD diastereomers, respectively. Workstation was Analyst 1.4.1 version.

2.5.3.2 Niagara River Suspended Sediment Samples

Analysis of HBCD in suspended sediments from Niagara River was performed using LC-ESI-MS/MS system at Environment Canada. See below for details.

HBCDs were injected and separated with an Agilent 1200 LC system comprising an Agilent 1200 Binary pump, Agilent 1200 high performance auto-sampler and Agilent 1200 thermostatically column compartment (column oven temperature set at 27℃), equipped with an Agilent Zorbax Eclipse Plus C_{18} column (2.1 mm x 100 mm; 3.5 µm). The workstation software was Analyst version 1.5.2 and the injection volume was 5 uL. A mobile phase program based upon (A) water/acetonitrile (1:1, v:v) and (B) methanol at a flow rate of 0.25 mL min^{-1} was applied for the elution of HBCD isomers; starting at 60% (B) for 4 min, then linearly increased to 100% (B) over 3 min and held for 5 min, then programmed linearly to 60% (B) over 3 min, and held for 7 min.

HBCD isomers were analysed using an AB Sciex QTRAP 4500 System equipped with an ESI source operated in negative ion mode. Ion transactions of m/z 640.7/78.9, m/z 652.7/78.9, and m/z 657.7/78.9 were detected in the multiple reaction monitoring mode (MRM) for quantification of native, $^{13}C_{12}$-, and d_{18}-HBCD isomers, respectively.

2.5.4 Analysis of NBFRs via GC-EI-MS/MS

The target NBFRs (see Table 2.4) in sediment samples were separated on a DB-5 MS column (15 m x 0.25 mm x 0.1 µm) fitted in an Agilent GC 7890A chromatograph, interfaced with an Agilent 7000 triple quadropole mass spectrometer detector (TQD). 1µL sample was injected using a 7693 Agilent auto-sampler at pulsed splitless injection mode using a multimode injector. Injector program was 90 ˚C for 0.02 min, and then increased to 300 ˚C at 700 ˚C min^{-1}; hold for 32.5 min. Helium was used as carrier gas at a constant flow rate of 1.2 mL min^{-1}. The initial oven temperature was 90 ˚C for 0.99 min, increased to 310 ˚C at a rate of 10 ˚C min^{-1}, held for 13 min, then increased post run to 315 ˚C and held for 3 min. Temperatures were set at 300 ˚C, 300 ˚C, and 150 ˚C for the transfer line, source and triple quadropole,

respectively.

2.6 Method Validation & Quality Assurance/Quality Control

2.6.1 Analyte Identification & Quantification Criteria

The elution orders of all target compounds were well known based on previous work conducted by our research team or relevant collaborators. Full five point calibration curves used to evaluate the linearity of the MS response were made with various concentration ranges for different sets of compounds, depending on their detection limits and signal responses. Calibration standards contained the same $^{13}C_{12}$-labelled standards as those spiked into samples prior to extraction, and the native compounds targeted in this study. Relative response factors (RRFs) were calculated using the peak areas from each five point calibration curves. The RRF is defined as the instrument response for a unit amount of target pollutant relative to the instrument response obtained for the same amount of the IS, and is calculated using equation 2.4.

$$RRF = A_{NAT}/A_{IS} * C_{IS}/C_{NAT} \qquad (2.4)$$

Where A_{NAT} is the peak area for the native compound; A_{IS} is the peak area of the isotopically (^{13}C- or d_{18}-) labelled internal standard; C_{NAT} is the concentration of the native compound while C_{IS} is the concentration of the internal standard. The relative standard deviations (RSDs) of the RRFs calculated for each target compound in the calibration curve were within 5%.

A single calibration standard of medium concentration was injected alongside approximately each 5 sample injections, with average RRFs calculated. These calculated RRFs have to be within ±25% of the average RRFs from the regularly checked 5 point calibration curve, which is used for the calculation of target compounds in samples, using Equation 2.5

$$Concentration = A_{NAT}/A_{IS} /RRF* M_{IS}/SS \qquad (2.5)$$

Where A_{NAT} and A_{IS} are the peak areas of the native and internal standard in the sample, respectively; RRF is the relative response factor for the target compound, as defined; M_{IS} is the mass of the internal standards added into the sample prior extraction; and SS refers to the sample size (with units of g, L, etc).

The following criteria must be met to quantify a given peak as an analyte in a sample:

1. The signal to noise ratio (S/N) must exceed 3:1;

2. The retention time of the peak in the sample under the same GC conditions must be within ±0.2% of those determined for the same compound in the calibration standard ran in the same sample batch.

3. The bromine isotope ratios must be within ±20% of the average for the calibration standards ran in the same sample batch.

2.6.2 Accuracy &Precision

The accuracy and precision of the water sample analysis was tested via triplicate analysis of NIST SRM2585 (standard reference material, House Dust). The results shown in Table 2.6 show very good agreement with certified or indicative values, alongside good precision. Note that quantification of HBCDs in Niagara River suspended sediments was conducted via the external standard method as HBCDs were not included in the original study remit. Consequently, appropriate internal standards were not added to the samples at the time of their original extraction, and recoveries for HBCDs could not be calculated. Instead, some measure of analyte recovery was obtained from calculation of the recoveries of the $^{13}C_{12}$-labelled BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-209 standards added to the original samples at point of extraction. The recoveries of these internal standards ranged from 91.5 to 107% with an average value of 97.4%.

Table 2.6 Concentrations of PBDEs, and PCBs in replicate analyses of NIST SRM2585 (house dust) compared to the certified values (ng g^{-1}), and recoveries for IS from recovery experiments

Compound	Ave. Con± SD	Certified Con.	Recoveries ± σ_{n-1}	
BDE 17	15.6 ± 0.15	11.5 ± 1.2	**^{13}BDE 28**	77 ± 11
BDE 28	56.2 ± 1.1	46.9 ± 4.4		
BDE 49	49.4 ± 2.5	53.5 ± 4.2	**^{13}BDE 47**	75 ± 7.0
BDE 47	628 ± 24	497 ± 46		
BDE 66	14.7 ± 1.5	_		
BDE 100	158 ± 1.7	145 ± 11	**^{13}BDE 99**	86 ± 29
BDE 99	996 ± 9.1	892 ± 53		
BDE 85	44.1 ± 0.26	43.8 ± 1.6		
BDE 154	93.3 ± 3.09	83.5 ± 2.0	**^{13}BDE 153**	65 ± 5.0
BDE 153	144 ± 3.61	119 ± 1		
PCB 28	12.3 ± 1.5	13.4 ± 0.5	**PCB 34**	110 ± 20
PCB 52	23.4 ± 4.7	21.8 ± 1.9	**PCB 62**	96 ± 9.3
PCB 101	23.4 ± 0.6	29.8 ± 2.3	**PCB 119**	107 ± 28
PCB 118	31.8 ± 1.7	26.3 ± 1.7	**PCB 131**	136 ± 35
PCB 180	24.7 ± 1.6	18.4 ± 3.2	**PCB 173**	111 ± 25
α- HBCD	21 ± 2.9 [a]	19 ± 3.7 [b]	**^{13}C-α- HBCD**	74-102 [a]
β- HBCD	4.1 ± 0.7 [a]	4.3 ± 1.1 [b]	**^{13}C-β- HBCD**	78-96 [a]
γ- HBCD	127 ± 16 [a]	120 ± 22 [b]	**^{13}C-γ- HBCD**	72-99 [a]

[a] Experimental results from replicate analysis (n=10) of NIST SRM 2585 spiked with $^{13}C_{12}$-α-, β-, and γ- HBCD

[b] Indicative HBCD concentration values reported by Keller et al. (2007)

2.6.3 Analysis of Blanks, LODs & LOQs

Water Samples For the first 6 batches of water samples, two types of blanks were assessed: (a) method blanks whereby two pre-cleaned PUFs and one baked and DCM rinsed GFF were treated as a sample; and (b) procedural field blanks. The latter comprised two pre-cleaned PUFs and one baked and DCM rinsed GFF through which 20 L Milli Q water were passed. For the remaining 7 batches of samples, only procedural field blanks conducted. The presence of target compounds in both blank categories was infrequent, and where detected, were less than 5% of the concentrations detected in the vast majority of samples. Thus no blank correction was made for water samples.

Lake Sediment Core Samples A method blank containing the same amount of sodium sulfate and hydromatrix as used for the analysis of English sediment samples was conducted alongside each batch of 11 samples. None of the target PCBs, PBDEs, and HBCD was found at detectable levels in method blanks.

Additionally, one extra sediment slice from the bottom of each sediment core from EDGB, MARM, PFLE, SLT and WAKE lakes (where core length permitted) were analysed to provide an estimate of the "background" contamination/interference levels in the lake sediment accumulated before the onset of production and usage of our target compounds.

Niagara River Suspended Sediment Samples Concentrations of the native HBCDs in the method blanks (n=4 in total) prepared for the Niagara River suspended sediment samples were only just above instrumental detection limits and <5% of the concentrations in the samples. Hence no blank correction was made to these data.

LODs and LOQs Instrumental limits of detection (LODs) were calculated for each of the target compounds based on a 3:1 signal to noise ratio, and were around 1 pg on column for PCB congeners; 0.4, 0.3, and 0.6 pg injection^{-1} for α-, β-, and γ-HBCD, respectively; 0.4, 0.3, 0.3, 0.1, 0.3, 0.3, 0.3, 0.5, 0.3, 0.3, 16.2 and 16.7 pg on column for BDE 17, 28, 49, 47, 66, 100, 99, 85, 154, 153, 183, and 209, respectively; 54, 1.0, 2.0, 51, 0.64, 12, 1.60, 1.60, 0.40, 0.50, 6.88, 0.40, and 0.40 pg on column for TBPH, PBEB, TBB, TBBPA-DBDPE, BTBPE, DBDPE, HCDBCO, TBECH, HBB, PBCC, PBBB, sDP, and aDP, respectively. Method limits of quantification (LOQs) in samples were based on a 10 times signal to noise ratio, taking into account average internal standard recoveries, the proportion of the final extract volume analysed, and the sample size.

***LOQs for Water Samples*:** 2 pg L^{-1} for individual PCB congeners; 0.4, 0.3, and 0.5 pg L^{-1} for α-, β-, and γ-HBCD respectively; and 0.8, 0.6, 0.6, 0.2, 0.8, 0.7, 0.6, 1.2, 1.0 and 0.9 pg L^{-1} for BDE 17, 28, 49, 47, 66, 100, 99, 85, 154, and 153, respectively.

***LOQs for Sediment Samples*:** The method detection limits were 0.001, 0.001, 0.002 ng g^{-1} dw for α-, β-, and γ-HBCD, respectively; 0.003-0.05 ng g^{-1} dw for BDE congeners; around 0.03 ng g^{-1} dw for PCB congeners; and 0.34, 0.01, 0.01, 0.32, 0.004, 0.07, 0.01, 0.01, 0.003, 0.003, 0.04, 0.003, and 0.003 ng g^{-1} dw for TBPH, PBEB, TBB, TBBPA-DBDPE, BTBPE, DBDPE, HCDBCO, TBECH, HBB, PBCC, PBBB, sDP, and aDP, respectively.

Regarding the Niagara River suspended sediment samples, the LODs for individual HBCD diastereomers were as low as the high fg level, offering satisfactory LOQs for analysis of HBCDs in these samples.

2.7 Statistical Analysis

In all instances, where analyte peaks were below instrumental detection limits, analyte concentrations are reported as non-detected. Statistical analysis of the data in this study was conducted using both Excel (Microsoft Office 2007) and IBM SPSS Statistics (version 21). Excel was used for basic descriptive statistics, e.g., calculations of mean, median, minimum, and maximum values, percentage contributions of individual congeners/diastereomers, generating linear regression charts, etc. Statistical analysis such as ANOVA, correlation analysis, multiple linear regressions, independent t-test, paired t-test, levels of significance, principal component analysis (PCA), were conducted via SPSS.

Chapter III

PCBs and "Legacy" BFRs in English Lake Water

3.1 Synopsis

Concentrations of PCBs and "legacy BFRs" (classified here as tri- to hexa-BDEs and HBCDs) are determined in water samples taken from 9 English freshwater lakes on 13 occasions between April 2008 and February 2012 (HBCDs were not determined in the first sample batch). Temporal, spatial, and seasonal trends in concentrations of the target compounds expressed on both a water-volume and TSS content basis are investigated with comparisons made with other studies where available. Correlations between concentrations of the target compounds and factors such as lake water temperature, sampling season, TSS content, population density, lake area, lake catchment area, and lake catchment ratio are studied. The congener profiles of PCBs and PBDEs, and the HBCD diastereomer pattern in water samples are reported and compared, both with data from other aquatic studies, and with commercial formulations for source attribution purposes. The influence on congener/diastereomer profiles, of potential influencing factors like total PCB, PBDE and HBCD concentrations, season, and TSS contents is also investigated.

Note that concentration data for all analytes and samples in batches with sampling dates between April 2008 and April 2010 inclusive were provided by Mrs Catalina Ibarra de Moore, Dr. Mohamed Abou-Elwafa Abdel-Ghalil Abdallah, and Dr. Jennifer Desborough. The author conducted all other chemical analyses and the interpretation of the data.

3.2 POPs Concentrations in Water Samples

3.2.1 PCB Concentrations

Concentrations of ΣPCBs in this study ranged from 40 to 390 pg L^{-1}, with individual site arithmetic mean values ranging from 79 to 210 pg L^{-1} (see Table 3.1, with concentrations normalised to TSS also reported). When compared with the USEPA guideline for PCBs for surface water of 14 ng L^{-1} (USEPA, 2002); PCB contamination levels in all of the nine monitored English freshwater lakes were well within acceptable levels, and are thus considered to pose no significant hazard to both aquatic and human health.

As summarised in Table 3.2, in an international context, concentrations of PCBs in seawater

are generally much lower than those reported in lake water in this study. This is likely attributable to dilution of the PCB burden in the much greater seawater volume. Compared to data available for various European freshwater bodies, the PCB contamination levels in our English freshwater lakes are moderate.

Outside Europe, ΣPCB concentrations in the Great Lakes are comparable with our data; while concentrations of PCBs in Mississippi river water, in New Orleans, Louisiana, USA are approximately three orders of magnitude higher than those in our study. Finally, PCB concentrations in river runoff and lakes in China were generally higher than those recorded in this study.

Table 3.1 Concentrations of ΣPCBs[a] in water expressed on both a water volume (pg L^{-1}) and TSS normalised basis (pg mg^{-1}, in parentheses) in English lakes

Location \ Date	Apr/08	Jul/08	Nov/08	Jan/09	Apr/09	Jul/09	Oct/09	Jan/10	Apr/10	Jul/10	Feb/11	Jul/11	Feb/12	Average Concentration $\pm\sigma_{n-1}$
CHAP	100 (12)	100 (9.7)	120 (17)	99 (27)	110 (14)	130 (9.2)	120 (8.2)	51 (9.0)	47 (3.5)	84 (8.2)	71 (7.8)	72 (5.3)	91 (48)	92±26 (14±12)
CRAZ	110 (38)	70 (21)	82 (12)	79 (22)	77 (86)	86 (23)	88 (63)	64 (49)	77 (38)	100 (8.0)	69 (5.1)	52 (11)	76 (30)	79±15 (31±24)
EDGB	74 (93)	91 (22)	110 (17)	120 (27)	100 (11)	110 (54)	190 (130)	40 (7.2)	73 (26)	74 (23)	120 (15)	69 (21)	130 (9.1)	100±37 (35±37)
HOLT	170 (290)	84 (140)	100 (60)	99 (45)	95 (68)	110 (63)	110 (52)	46 (26)	76 (64)	63 (42)	81 (74)	53 (20)	78 (41)	90±31 (76±71)
MARM	140 (120)	170 (43)	190 (64)	180 (75)	170 (62)	190 (130)	210 (130)	86 (16)	130 (60)	73 (12)	90 (11)	51 (39)	90 (60)	140±53 (63±42)
PFLE	110 (3.3)	130 (2.5)	150 (7.2)	150 (6.8)	130 (2.7)	140 (2.7)	110 (5.5)	91 (4.8)	110 (2.9)	150 (2.6)	120 (2.4)	130 (3.2)	100 (12)	130±20 (4.5±2.8)
SLT	290 (130)	220 (26)	260 (320)	250 (33)	230 (130)	260 (73)	220 (150)	94 (32)	78 (19)	110 (4.0)	71 (12)	74 (3.9)	82 (27)	170±87 (74±90)
THOP	99 (4.9)	320 (260)	370 (21)	360 (25)	350 (38)	370 (340)	73 (29)	68 (13)	- [b]	100 (49)	190 (10)	71 (47)	150 (14)	210±130 (71±110)
WAKE	390 (74)	85 (7.6)	110 (12)	120 (26)	100 (27)	110 (40)	140 (40)	69 (24)	140 (28)	100 (29)	78 (17)	49 (11)	89 (19)	120±85 (27±17)

[a] Sum of PCB 28, 52, 101, 118, 153, 138, and 180

[b] One sample for THOP was missing due to drought on this sampling occasion

Table 3.2 A comparative summary of the concentrations (average) of PCBs (pg L^{-1} unless denoted otherwise) in various water bodies, with an emphasis on lakes

Location	Target PCB Congeners	Dissolved Phase	Particulate Phase	Bulk Water	Reference
European Water Bodies					
Nine English freshwater Lakes (n=116)	*CB 28, 52, 101, 118, 153, 138, and 180*			*40-390 (79-210)*	*Current study*
Esthwaite Water, a small lake in Cumbria, UK	CB 28, 52, 101, 118, 153, 138, and 180	Average 1808			Gevao et al., 1998
Lake water and tributary river water from Lake Thun, Switzerland	CB 28, 52, 101, 138, 153, and 180			16 to 80	Bogdal et al., 2010
Kerkini Lake, the Strymon River, its main tributaries and estuary in N. Aegean Sea, Greece	CB 28, 52, 101, 138, 153, and 180			n.d.-162 ng L^{-1}	Litskas et al., 2012
Three European remote mountain lakes	CB 28, 52, 101, 118, 138, 153, and 180			26-110	Vilanova et al., 2001
Seine river basin, France	Sum of 21 PCB congeners			4300-8700	Teil et al., 2014
	CB 28, 52, 101, 118, 138, 153, and 180			2600-4800	
Water-column from the Seine Estuary, France	A selection of PCB congeners (CB 8 - CB 209)	2.0-21.2 (7.0) ng L^{-1}	58-463 (227) ng g^{-1}	14.1-55.0 (26.1) ng L^{-1}	Cailleaud et al., 2007
Venice lagoon water	Sum of 49 PCB congeners	250-792	105-1273	355-1868	Moret et al., 2005
Baltic seawater	CB 28, 31, 101, 118, 138, 149, 153, and 180	0.1 - 4.5	0.2 - 7.1		Bruhn and McLachlan, 2002
Outside Europe					
Lake Michigan water	Sum of 110 chromatographic peaks	average 150 (n=7)	average 28 (n=6)		Streets et al., 2006

Location	Target PCB Congeners	Dissolved Phase	Particulate Phase	Bulk Water	Reference
Mississippi river, New Orleans, Louisiana, USA	Sum of 28 PCB congeners (CB 1 to nona-CBs)			22.2-163.4 (86.5) ng L^{-1}	Zhang et al., 2007
Eight riverine runoff outlets of the Pearl River Delta	Sum of 20 PCB congeners			120-1470 (770)	Guan et al., 2009
A river affected by wastewater treatment effluent, Beijing, China (2010)	Sum of 26 PCB congeners (CB 3 - CB 209)			174	Yu et al., 2013
Pearl River Estuary, China	CB 4, 15, 16, 17, 18, 22, 28, 37, 56, 66, and 70	18.0-7180	21.3-14700		Chen et al., 2011
Dianchi Lake, China	CB 28, 52, 101, 138, 153 and 180			13-72 (44) ng L^{-1}	Wan et al., 2011
Tonghui River, China	Sum of 12 PCB congeners			31.6-345 ng L^{-1}	Zhang et al., 2004

3.2.2 PBDE Concentrations

Table 3.3 shows concentrations of ΣBDEs in this study ranged from 9.2 to 170 pg L^{-1}, with concentrations normalised to TSS also shown. This is, to the best knowledge of the author, the first report on PBDE concentrations in English lake water. The tri- through hexa-BDEs that comprise the Penta-BDE formulation were listed collectively as a priority hazardous substance in the Water Framework Directive (WFD, Directive 2013/39/EU), with the aim to cease or phase out its discharges, emissions and losses. The environmental quality standard (EQS, Directive 2008/105/EC) for maximum allowable concentration of Σtri-hexa-BDEs for inland surface freshwater is 140 ng L^{-1}. PBDE concentrations in our nine English lakes are far below this EQS.

As summarised in Table 3.4, concentrations of PBDEs in English lake water are similar to those reported previously for other European lakes. Moreover, even when a wider geographic scale is considered, the concentrations reported in our study are comparable and largely consistent with levels obtained elsewhere for various water bodies, except where samples were taken in heavily source-impacted areas.

Interestingly, our data for English lakes are comparable with those reported for the USA (Streets et al., 2006; Sacks and Lohmann, 2012) in spite of the far greater production of the Penta-BDE product in the Americas than Europe. While this contrasts with the higher PBDE concentrations observed in North American house dust compared to the UK (Harrad et al., 2008b), it is consistent with similar concentrations of PBDEs in outdoor air in the USA and the UK (Harrad and Hunter, 2006; Harrad et al., 2004; Gouin et al., 2005). The cause(s) of these somewhat conflicting observations are not clear at this time, but we note that the UK has a substantially higher population density than the US, which means that Penta-BDE use in the UK and the USA may actually be similar when normalised to surface area. Moreover, concentrations in the Great Lakes will be subject to a far greater dilution factor owing to their far greater volume than the lakes in our study.

Table 3.3 Concentrations of ΣBDEs[a] in water expressed on both a water volume (pg L^{-1}) and TSS normalised basis (pg mg^{-1}, in parentheses) in English lakes

Location \ Date	Apr/08	Jul/08	Nov/08	Jan/09	Apr/09	Jul/09	Oct/09	Jan/10	Apr/10	Jul/10	Feb/11	Jul/11	Feb/12	Average Concentration $\pm\sigma_{n-1}$
CHAP	17 (2.0)	74 (7.1)	74 (11)	72 (20)	71 (8.8)	87 (6.4)	65 (4.7)	64 (12)	75 (5.5)	55 (5.4)	22 (2.5)	15 (1.1)	62 (33)	58±24 (9.2±8.7)
CRAZ	21 (7.4)	70 (22)	72 (10)	83 (24)	66 (73)	83 (23)	79 (56)	87 (67)	73 (37)	140 (11)	59 (4.4)	9.2 (1.9)	75 (31)	71±31 (28±24)
EDGB	15 (19)	57 (14)	63 (9.5)	73 (17)	66 (7.2)	51 (26)	54 (40)	61 (11)	87 (32)	47 (15)	39 (5.1)	14 (4.3)	150 (11)	60±34 (16±11)
HOLT	29 (49)	60 (99)	58 (35)	68 (31)	63 (45)	67 (41)	72 (35)	80 (45)	67 (58)	53 (36)	29 (26)	49 (19)	53 (28)	58±15 (42±20)
MARM	17 (15)	42 (11)	44 (15)	57 (24)	47 (18)	56 (40)	60 (37)	72 (14)	56 (27)	59 (10)	91 (11)	55 (43)	61 (42)	55±17 (24±13)
PFLE	16 (0.5)	61 (1.2)	73 (3.4)	89 (4.1)	79 (1.6)	89 (1.7)	70 (3.5)	87 (4.6)	110 (2.8)	72 (1.2)	84 (1.6)	48 (1.2)	73 (8.4)	73±23 (2.8±2.1)
SLT	42 (19)	60 (7.3)	56 (75)	65 (8.7)	57 (32)	69 (20)	130 (89)	91 (32)	85 (20)	85 (3.0)	31 (5.1)	24 (1.3)	90 (30)	68±29 (26±27)
THOP	15 (0.7)	44 (35)	50 (2.9)	57 (4.1)	56 (6.2)	61 (58)	- [b]	120 (24)	- [c]	73 (36)	170 (9.0)	21 (14)	140 (13)	73±49 (18±18)
WAKE	33 (6.3)	45 (4.0)	42 (4.3)	46 (10)	40 (11)	47 (18)	53 (15)	59 (20)	52 (11)	38 (11)	18 (3.8)	14 (3.0)	53 (11)	42±13 (9.9±5.5)

[a] Sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153

[b] This sample was lost during analysis

[c] This sample was missing due to drought on this sampling occasion

Table 3.4 A comparative summary of the concentrations (average) of PBDEs (pg L^{-1}) in various water bodies, with an emphasis on lakes

Location	Target BDE Congeners	Dissolved Phase	Particulate Phase	Bulk Water	Reference
European Water Bodies					
Nine English freshwater Lakes (n=115)	*BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153*			*9.2 to 170 (42-73) (n=115)*	*Current Study*
Seine river basin, France	Σtri-hexa-BDEs			80-350	Teil et al., 2014
Scheldt Estuary and North Sea along the Dutch coast	BDE-47, -99, and -153			around 1.6	Booij et al., 2002
Lake Thun, Switzerland	Σtri-deca-BDEs			17-78	Bogdal et al., 2010
Outside Europe					
Lake Michigan	BDE-47, -99, -100, -153, -154 and -183			Increased from average 31 in 1997 to 158	Stapleton and Baker, 2001
Lake Michigan	BDE-47, -66, -99, -100, -153 and -154	Average 18	Average 3.1		Streets et al., 2006
Lake Winnipeg, Canada	BDE-47, -85, -99, -100, and -153	Average 29.5			Law et al., 2006
An urban estuary, Narragansett	BDE-47, -99, and -153			< 3	Sacks and Lohmann, 2012
San Francisco Bay	Same congeners as this study, except BDE-49			0.2 -299	Oros et al., 2005
San Francisco Bay	BDE-47			15.5 to 337 (54.9)	Oram et al., 2008
Zhujiang River estuary, China	BDE-28, -47, -100, -99, -153, -154 and -183			26.1-94.6 in May; 71.4-156.9 in October	Luo et al., 2008
Pearl River Estuary, China	BDE-28, -47, -66, -100, -99, -153, -154 and -183	7.0-127	6.2-77.6		Chen et al., 2011
A reservoir at an e-waste recycling area, China	BDE-28, -47, -100, -99, -138, -153 and -154			Average 21.8 ng L^{-1}	Wu et al., 2008

3.2.3 HBCD Concentrations

Concentrations of total HBCDs (sum of α-, β-, and γ-HBCD) in water in this study ranged from 45 to 890 pg L^{-1} (see Table 3.5), with the highest and lowest average ΣHBCDs concentrations found at EDGB (230 pg L^{-1}) and WAKE (110 pg L^{-1}), respectively. HBCD was recently listed as a priority hazardous substance in the WFD (Directive 2013/39/EU), with environmental quality standards for the annual average and maximum allowable concentration for inland surface freshwater of 1.6 ng L^{-1} and 500 ng L^{-1}, respectively. HBCD concentrations in our nine English lakes did not exceed these levels.

Reports on HBCD concentrations in freshwater are extremely rare; the few comparative data of which we are aware are: HBCD was detected at frequencies of 100% in freshwater (n=5) and sea water (n=5) sampled in 2012 from the aquatic environment of Denmark, with concentrations ranged from 96 to 2900 pg L^{-1}, and 52 to 400 pg L^{-1}, respectively, with HBCD concentrations in freshwater slightly higher than in our English freshwater lakes (Vorkamp et al., 2014); Outside Europe, γ-HBCD was detected in 2 out of 12 water samples collected in 2010 from Taihu Lake, China at concentrations of 370 and 180 pg L^{-1}, respectively, while α-, and β-HBCD were not detectable (Xu et al., 2013). HBCD concentrations in Taihu Lake are comparable with our study but at much lower detection frequencies; HBCD concentrations in lake water, river water, and snow water (n=1 for each) from China were: <15, <5, and <10 ng L^{-1} for α-, β-, and γ-HBCD, respectively (Zhao et al., 2011a).

3.3 Partitioning of POPs between Dissolved and Particulate Phase

3.3.1Partitioning of PCBs

Table 3.6 reports the concentrations of target compounds determined separately in the particulate and freely dissolved phases in the July 2008 samples from each of the 9 sites, to provide information on their phase partitioning. The freely-dissolved phase in this study is operationally defined as that passing through a 1 μm pore size GFF. For total PCBs, 45-53% was found in the particulate phase (n=9), with an average$\pm\sigma_{n-1}$ value of 49±3%, indicating a generally equal proportion of PCBs in the freely dissolved and particulate phases in the bulk water. However, for individual PCB congeners, the average$\pm\sigma_{n-1}$ values of PCBs associated with the particulate phase were: 44±3%, 39±8%, 66±7 %, 62±11%, 63±9%, 70±13%, and 64±24% for PCB 28, 52, 101, 118, 153, 138, and 180, respectively. This indicates some dependence on the degree of chlorination, with higher chlorinated PCBs more strongly

associated with particulates. The plausible explanation is that, as illustrated in Figure 3.1, the higher chlorinated PCB congeners display greater potential for binding to the particulate phase, due to their higher Log K_{OW} values.

It should be noted that this batch of samples were taken in summer, with individual site temperatures (measured at 50 cm below the water surface) ranging from 14-23 ˚C (average 19 ˚C), which likely enhances partitioning towards the dissolved phase compared to colder seasons. In addition, other environmental factors can influence the partitioning of PCBs between the dissolved and suspended sediment phases. For example, seasonal dependence has been reported in a study of the Pearl River Estuary, with dissolved phase concentrations lower than those in the particulate phase in May and July (flood season), but higher in October (dry season) (Chen et al., 2011). The authors hypothesised that this was due to seasonal changes in the suspended particulate matter (SPM) content. Specifically, higher SPM concentrations in the flood season were suggested to be driving the higher proportion of PCBs in the suspended sediment phase.

Consistent with our observations, higher contributions of PCB 28 and 31 in the dissolved phase and PCB 138 and 153 in the particulate phase was found in Baltic seawater (Bruhn and McLachlan, 2002). In contrast however, ΣPCB concentrations (sum of 110 chromatographic peaks) in Lake Michigan water sampled in April and July in 2004 were on average 150 and 28 pg L^{-1} in dissolved (n=7) and particulate phase (n=6) respectively (Streets et al., 2006).

Table 3.5 Concentrations of ΣHBCDs[a] in water expressed on both a water volume (pg L^{-1}) and TSS normalised basis (pg mg^{-1}, in parentheses) in English lakes

Location \ Date	Jul/08	Nov/08	Jan/09	Apr/09	Jul/09	Oct/09	Jan/10	Apr/10	Jul/10	Feb/11	Jul/11	Feb/12	Average Concentration $\pm\sigma_{n-1}$
CHAP	120 (11)	140 (20)	190 (54)	150 (19)	130 (9.3)	200 (15)	140 (24)	150 (11)	140 (14)	150 (17)	45 (3.3)	88 (47)	140±55 (20±15)
CRAZ	95 (29)	110 (16)	130 (38)	93 (100)	110 (31)	100 (74)	780 (600)	560 (280)	83 (6.4)	110 (8.3)	56 (12)	80 (32)	190±230 (100±170)
EDGB	240 (59)	260 (39)	310 (72)	240 (26)	270 (140)	170 (120)	160 (28)	360 (130)	69 (21)	450 (58)	60 (19)	120 (8.9)	230±130 (60±46)
HOLT	100 (170)	110 (64)	140 (64)	100 (72)	120 (70)	220 (100)	170 (95)	84 (70)	320 (210)	96 (87)	94 (36)	74 (39)	140±78 (90±51)
MARM	170 (43)	190 (64)	220 (91)	170 (64)	200 (150)	330 (210)	180 (34)	59 (28)	67 (11)	130 (15)	58 (45)	63 (42)	150±90 (66±59)
PFLE	72 (1.4)	94 (4.4)	190 (8.5)	87 (1.8)	92 (1.8)	69 (3.4)	220 (12)	130 (3.3)	200 (3.3)	210 (4.1)	92 (2.4)	53 (6.1)	130±69 (4.4±3.1)
SLT	250 (30)	280 (350)	290 (39)	280 (160)	300 (83)	96 (64)	140 (47)	590 (140)	96 (3.3)	130 (21)	60 (3.1)	58 (19)	210±160 (80±99)
THOP	72 (60)	78 (4.5)	90 (6.5)	83 (9.1)	110 (100)	110 (43)	890 (180)	- [b]	110 (51)	89 (4.7)	95 (64)	470 (44)	200±250 (52±52)
WAKE	88 (7.8)	100 (11)	110 (26)	94 (25)	130 (48)	78 (22)	100 (34)	120 (25)	200 (56)	190 (41)	61 (13)	61 (13)	110±53 (27±15)

[a] Sum of α-, β-, and γ-HBCD

[b] This sample was missing due to drought on this sampling occasion

Table 3.6 Concentrations (pg L^{-1}) and relative abundances (%, in parentheses) of target compounds in operationally-defined particulate (filters) and freely-dissolved phases (PUFs) of water samples taken in July 2008

Location	ΣPCBs		ΣPBDEs		ΣHBCDs	
	PUFs	Filters	PUFs	Filters	PUFs	Filters
CHAP	54 (53)	48 (47)	25 (34)	49 (66)	62 (73)	23 (27)
CRAZ	36 (51)	35 (49)	26 (37)	44 (63)	47 (87)	7.0 (13)
EDGB	50 (55)	41 (45)	13 (23)	44 (77)	110 (79)	29 (21)
HOLT	47 (55)	38 (45)	18 (31)	41 (69)	42 (70)	18 (30)
MARM	88 (52)	81 (48)	15 (36)	27 (64)	82 (80)	20 (20)
PFLE	60 (47)	69 (53)	21 (34)	41 (66)	33 (87)	5.0 (13)
SLT	110 (50)	110 (50)	18 (30)	42 (70)	110 (86)	18 (14)
THOP	150 (48)	160 (52)	14 (32)	30 (68)	28 (67)	14 (33)
WAKE	42 (49)	43 (51)	14 (31)	31 (69)	47 (84)	9.0 (16)

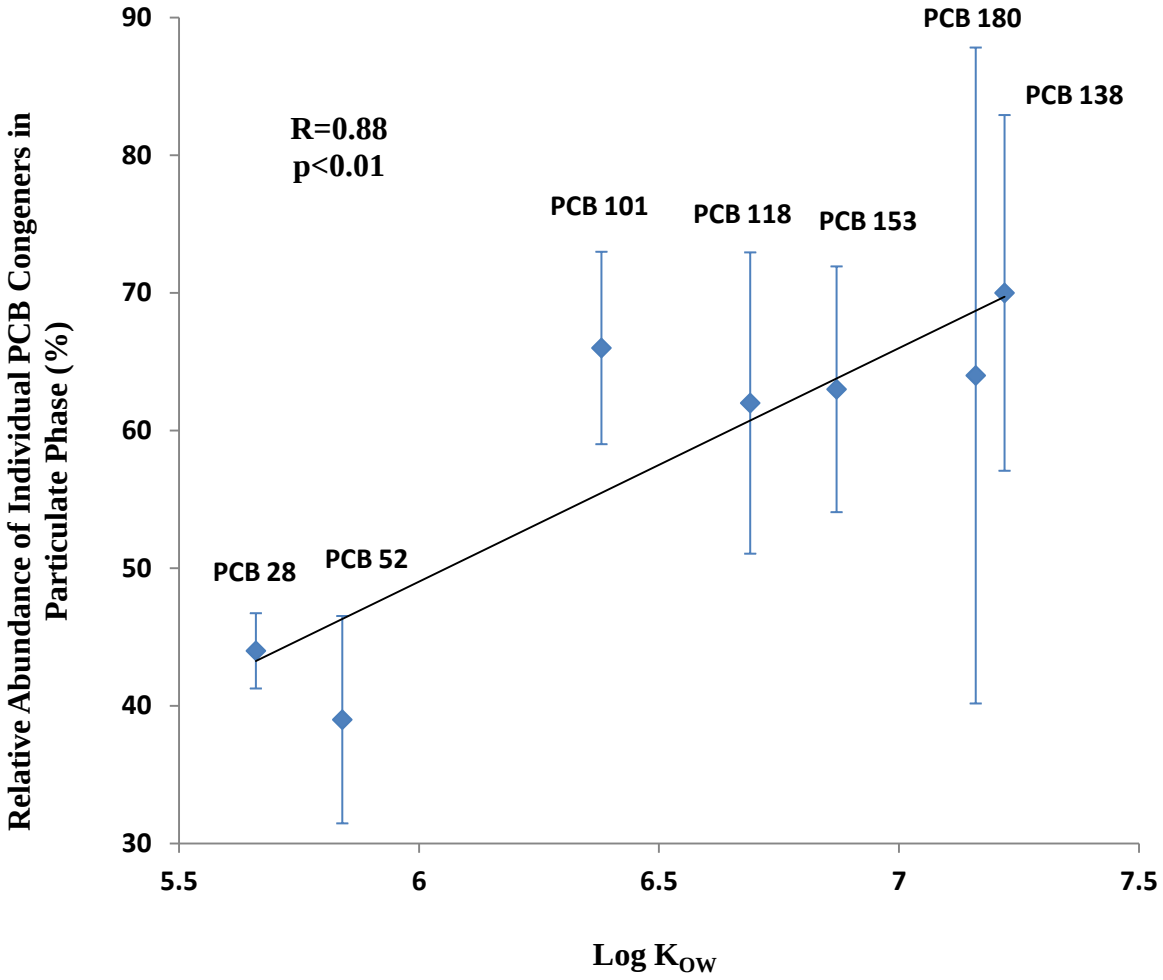


Figure 3.1 Relationship between Log K_{OW} and the average relative abundance (%; with standard deviation as y-error bar) of PCBs associated with particulate phase in samples taken in July 2008

3.3.2 Partitioning of PBDEs Across all nine samples, 63-77% of ΣBDEs were found in the particulate phase, with an average$\pm\sigma_{n-1}$ value of 68±6%. We could not investigate the relationship between the particulate-bound proportions of individual PBDEs and Log K_{OW}, as a result of the low detection rates of many BDE congeners in this study. In the only other study on this topic of which we are aware, Oros et al. (2005) reported that 78-93% of ΣBDEs (sum of 22 tri- through deca-BDE congeners) were present in the particulate phase of 3 water samples from the San Francisco estuary using an identical 1 µm cut-off to that used in this study. This is generally consistent with our findings, particularly given the inclusion of BDE-209 (which would skew the proportion of ΣBDEs bound to the particulate phase towards the high end) in the San Francisco study.

3.3.3 Partitioning of HBCDs

Across all sites, 47-61% of ΣHBCDs were found in the particulate phase, with an average$\pm\sigma_{n-1}$ value of 51±6%, 50±9%, 54±5%, and 53±5% for α-, β-, γ-, and ΣHBCDs, respectively; revealing no apparent diastereomer-specific differences in partitioning between the dissolved and particulate phases. This could be due to their very similar Log K_{OW} values (5.07, 5.12, and 5.47 for α-, β-, γ- HBCD, respectively). To the best of our knowledge, there are currently no other data available for comparison on the phase partitioning of HBCDs in either freshwater or seawater.

3.4 Factors Influencing POPs Concentrations

3.4.1 Influence of TSS

Influence of TSS on concentrations of PCBs The TSS content of samples collected from all sites in February 2011 was determined gravimetrically after filtration of the entire 40 L sample. Values ranged from 0.32 mg L^{-1} at HOLT to 46 mg L^{-1} at PFLE. As shown in Figure 3.2 (a), PCB concentrations (sum of both phases) showed some modest but not significant dependence on TSS (R=0.431, p=0.123, one-tailed, blue line). This was enhanced significantly however when the PFLE site was excluded (green line, R=0.694, $p<0.05$ one-tailed). This strong correlation demonstrates clearly the influence of TSS on PCB contamination. With respect to the PFLE site, although it exhibited PCB concentrations at the higher end of those recorded in this study, the concentration at this site was lower than expected given the high TSS content of samples from PFLE. One possible explanation for this is related to the fact that this site is known to suffer occasional episodes of cyanobacteria

(blue-green) algae. Sugiura (1992) reported microbial degradation of PCBs on suspended particulates in aquatic environments. Moreover, microbial transformation and degradation of PCBs in various environments including sediments has been highlighted by Field and Sierra-Alvarez (2008). While recognising that more detailed study is required to verify this, we therefore hypothesise that the occasional episodes of cyanobacteria at PFLE may have enhanced PCB degradation, thereby reducing the correlation between TSS and PCB concentrations at this site. However, TSS contents determined separately by collaborators at UCL for all samples using smaller volumes (~1 L) and likely subject to greater uncertainty) showed no statistically positive correlation with PCB concentrations across all samples in this study ($R=0.048$, $p>0.05$).

Influence of TSS on concentrations of PBDEs TSS content determined for all samples showed positive correlation with ΣBDE concentrations ($R=0.190$, $p<0.05$), indicating stronger TSS dependence of PBDEs than PCBs in this study. Such a strong correlation demonstrates clearly the influence of TSS on PBDE concentrations. Our findings are consistent with those of Oros et al. (2005), who reported a significant positive relationship between ΣBDE concentrations and TSS in San Francisco estuary. Moreover, when the February 2011 batch samples only were studied, for which TSS data was recorded for the entire 40 L sample volume; consistent with observations for PCBs, the dependence of ΣBDE concentrations on TSS ($R =0.462$, $p=0.105$, blue line, Figure 3.2 (b) was enhanced significantly when the PFLE site was excluded (green line, $R=0.873$, $P<0.01$). Moreover, as for PCBs, microbial transformation of PBDEs in marine sediments was confirmed by Martin et al. (2004). We therefore hypothesise that the occasional episodes of cyanobacteria at PFLE may also have enhanced PBDE degradation, thereby reducing the correlation between TSS and PBDE concentrations at this site.

Influence of TSS on concentrations of HBCDs In contrast to PCBs and PBDEs, HBCDs in this study showed no statistically significant correlation with TSS content either across all samples or in the February 2011 batch samples only (even when the PFLE site was excluded). It appears therefore, that unlike PBDEs and PCBs, the relationship between HBCD and TSS contents in our lake water samples is not significant.

3.4.2 Seasonal Variability in POPs Concentrations in Lake Water

There is clear potential for POPs concentrations in various environmental matrices to display seasonal variation given the variety of factors that may both influence POPs concentrations

and display seasonal variation. Examples include: water temperature, TSS content, and rainfall etc. This section therefore addresses seasonal variations in concentrations of POPs in English freshwater lake water and its causes. In this study, dates from March 21st to September 20th were defined as warmer periods with an average temperature of 16.4 ˚C; while dates from September 21st to March 20th were defined as colder periods with an average temperature of 6.4 ˚C.

Seasonal Variations in TSS Content Given our observation of a positive linear relationship between PCB and PBDE concentrations and TSS, we examined our data for any seasonal variation in TSS content. Any such variation could potentially help account for any seasonal variability in POPs concentrations. In line with a previous study of the River Seine (Cailleaud et al., 2007), we observed higher TSS contents (mean values) in colder compared to warmer periods at CRAZ, EDGB, HOLT, MARM, and THOP (by factors of 1.1, 1.8, 1.3, 1.4, and 2.3, respectively), see Figure 3.3. Such winter increments in TSS are likely attributable to greater re-suspension of sediment due to die-back of aquatic plants and increased mixing of the water column due to higher precipitation and wind speeds during colder periods. For CHAP, PFLE, SLT, and WAKE, TSS contents in colder period were lower than/equal to those in warmer period, by factors of 0.6, 0.5, 0.4, and 1.0, respectively.

Seasonal Impacts on PCB Concentrations No statistically significant correlation was apparent between PCB concentrations (on both a water-volume and TSS content basis) and water temperature recorded at the time of sampling across all samples. Moreover, a t-test showed no statistically significant differences between PCB concentrations in warmer and colder periods across all samples. This is not a surprise, given the other potential influences on concentrations between the different sites.

Furthermore, as shown in Figure 3.4 and 3.5, ΣPCB concentrations (on both water-volume and TSS content basis; average of 13 sample batches) at individual sites display no clear and consistent seasonal trends among sites ($p>0.05$ for both). This was replicated for individual PCB congeners with the exception of PCB-28, for which higher concentrations were observed in warmer than in colder periods ($p<0.05$).

Moreover, as shown in Figure 3.6 (a), there is no statistically significant relationship between the ratios of average ΣPCB concentrations at individual sites in colder relative to those in warmer periods, and the same seasonal ratios of average TSS contents. This suggests that the seasonal variability in TSS does not lead to a similar seasonal variation in concentrations of

ΣPCBs. Furthermore, multi-linear regression showed no statistically significant influence of TSS and season on PCB concentrations.

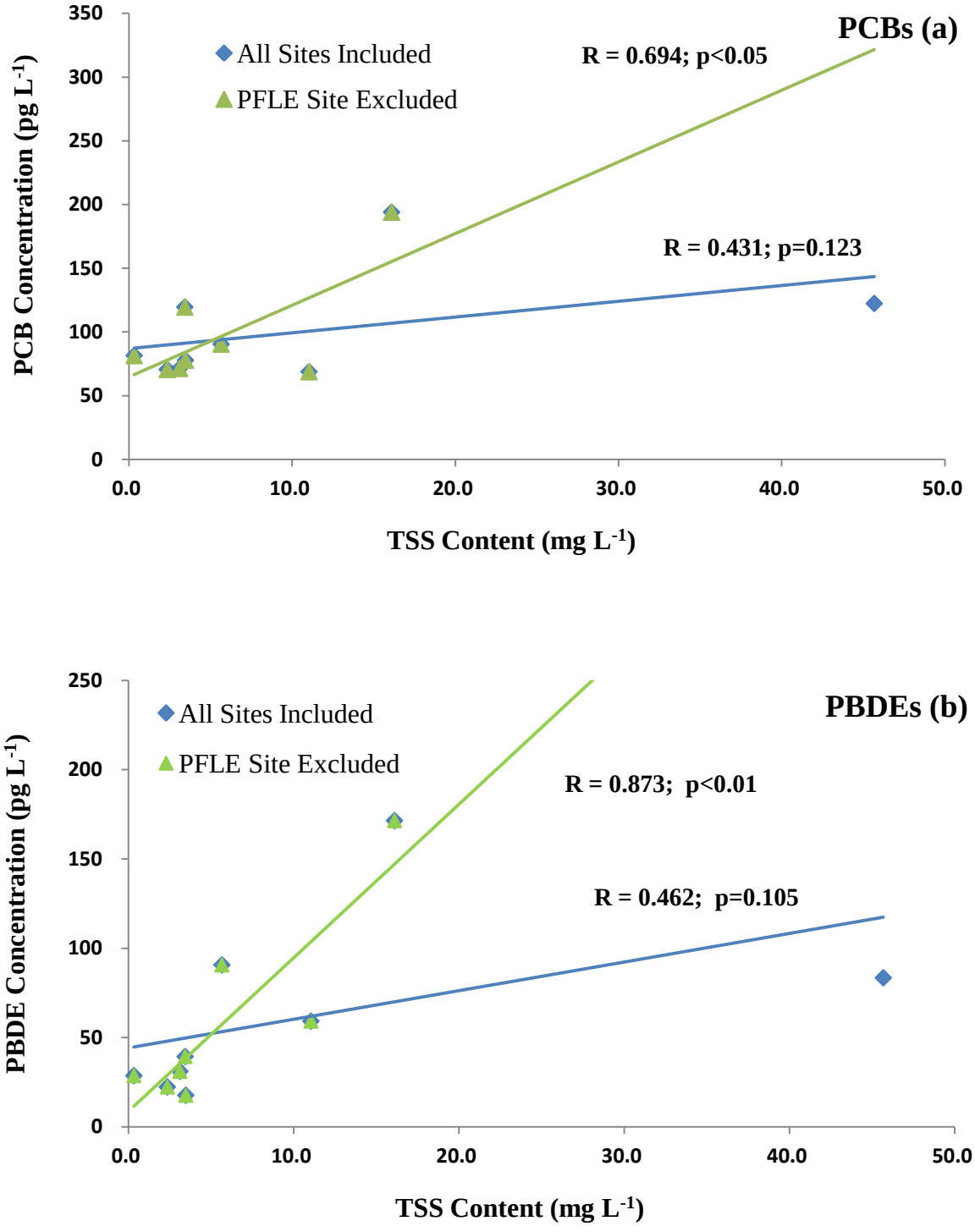


Figure 3.2 Correlations between TSS content (measured for February 2011 samples only) and: (a) PCB concentrations & (b) PBDE concentrations (sum of both phases; with and without PFLE Sites, blue and green lines, respectively)

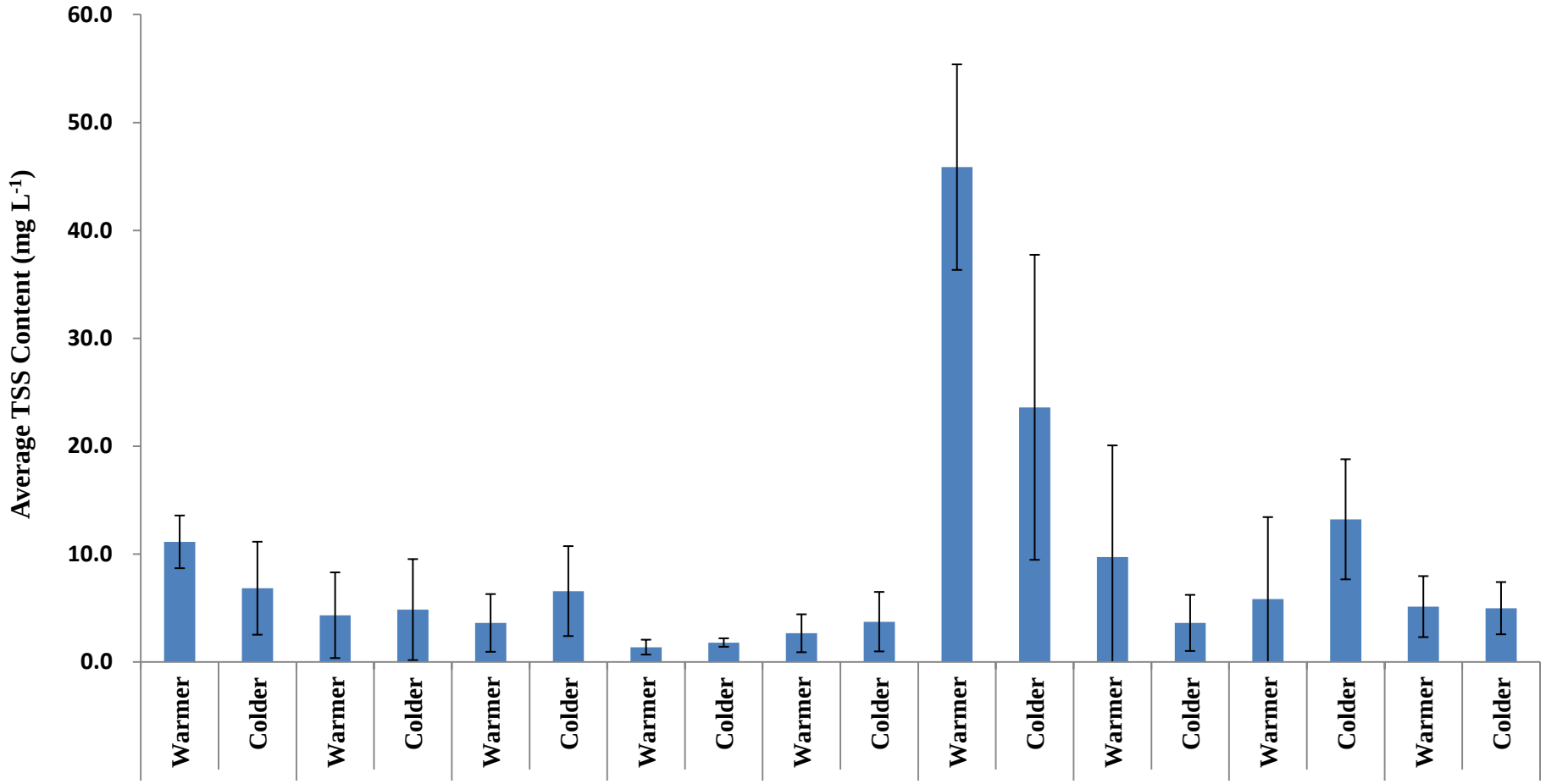


Figure 3.3 Average TSS Content (mg L^{-1}) in warmer and colder periods at each site over the monitored periods

To place our data in context, in other studies, concentrations of PCBs (sum of 20 PCB congeners) in water at eight riverine runoff outlets in the Pearl River Delta showed no seasonal trends (Guan et al., 2009). Dissolved phase concentrations of PCBs showed no seasonal trends in the Hudson River Estuary between December 1999 and April 2001 (Yan et al., 2008), nor in Baltimore Harbour and the Northern Chesapeake Bay in 1996-97 (Bamford et al., 2002). In contrast, the maximum PCB concentrations associated with TSS in water from the Seine Estuary were observed in winter periods over the period November 2002 to February 2005, while highest operationally-defined dissolved phase PCB concentrations were found in winters 2003 and 2004, and summer 2003 (Cailleaud et al., 2007).

Seasonal Impacts on concentrations of PBDEs As illustrated in Figure 3.7, PBDE concentrations expressed on a water volume basis over all sites were significantly elevated in colder compared to warmer periods ($p<0.05$). Concentrations of PBDEs expressed on a TSS content basis were also elevated in colder periods at most - but importantly not all - sites, see Figure 3.8 (independent sample t-test, $p>0.05$).

The seasonal increments in TSS in colder periods at CRAZ, EDGB, HOLT, MARM, and THOP corresponded with similar increments in average ΣBDE concentrations at the same sites in colder compared to warmer periods (factors of 1.1, 1.5, 1.1, 1.3, and 2.3, respectively). For these five sites therefore, the winter increment in PBDE contamination appears at least partly attributable to seasonal variations in TSS content. Moreover, as shown in Figure 3.6 (b), the ratios of average ΣBDE concentrations at individual sites in colder relative to those in warmer periods were significantly correlated with the same seasonal ratios of average TSS contents. This indicates the positive influence of TSS on PBDE concentrations in English lake water.

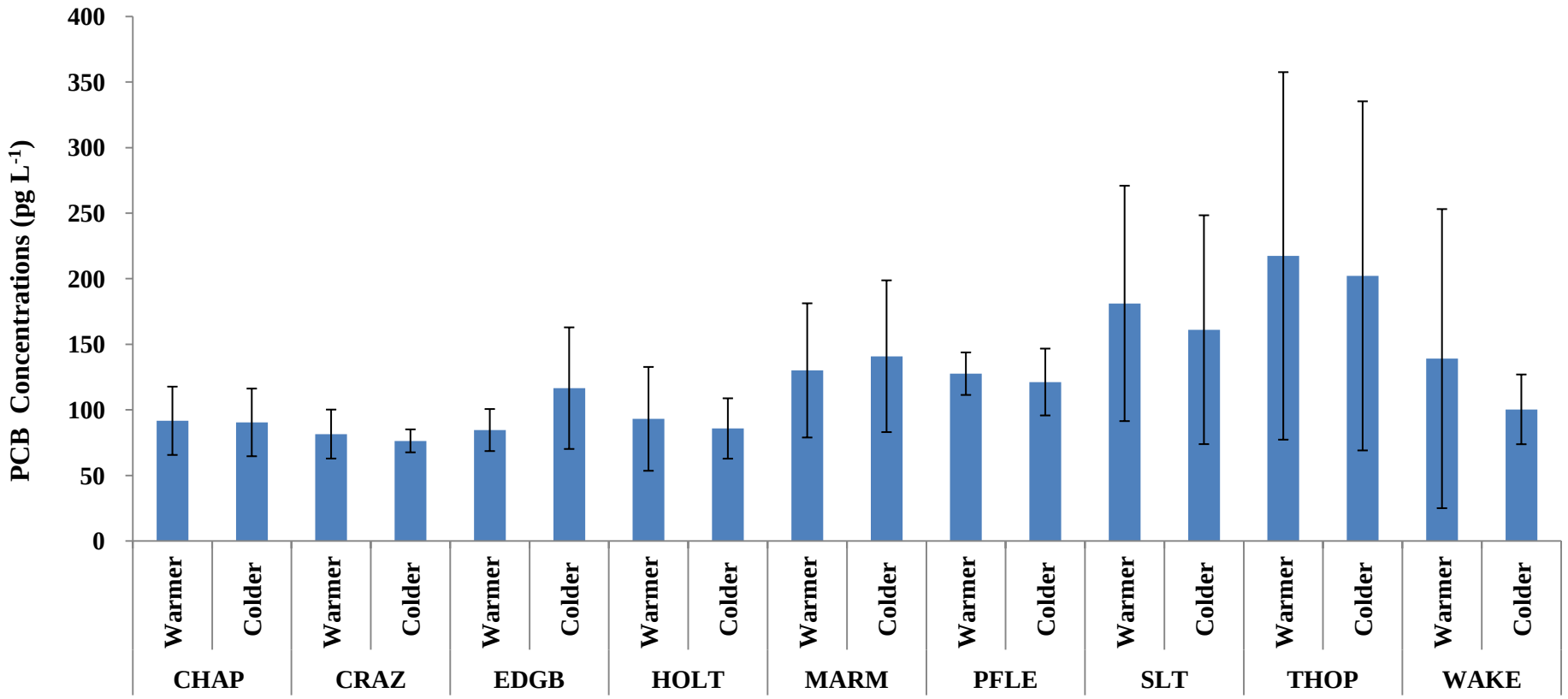


Figure 3.4 Average PCB concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

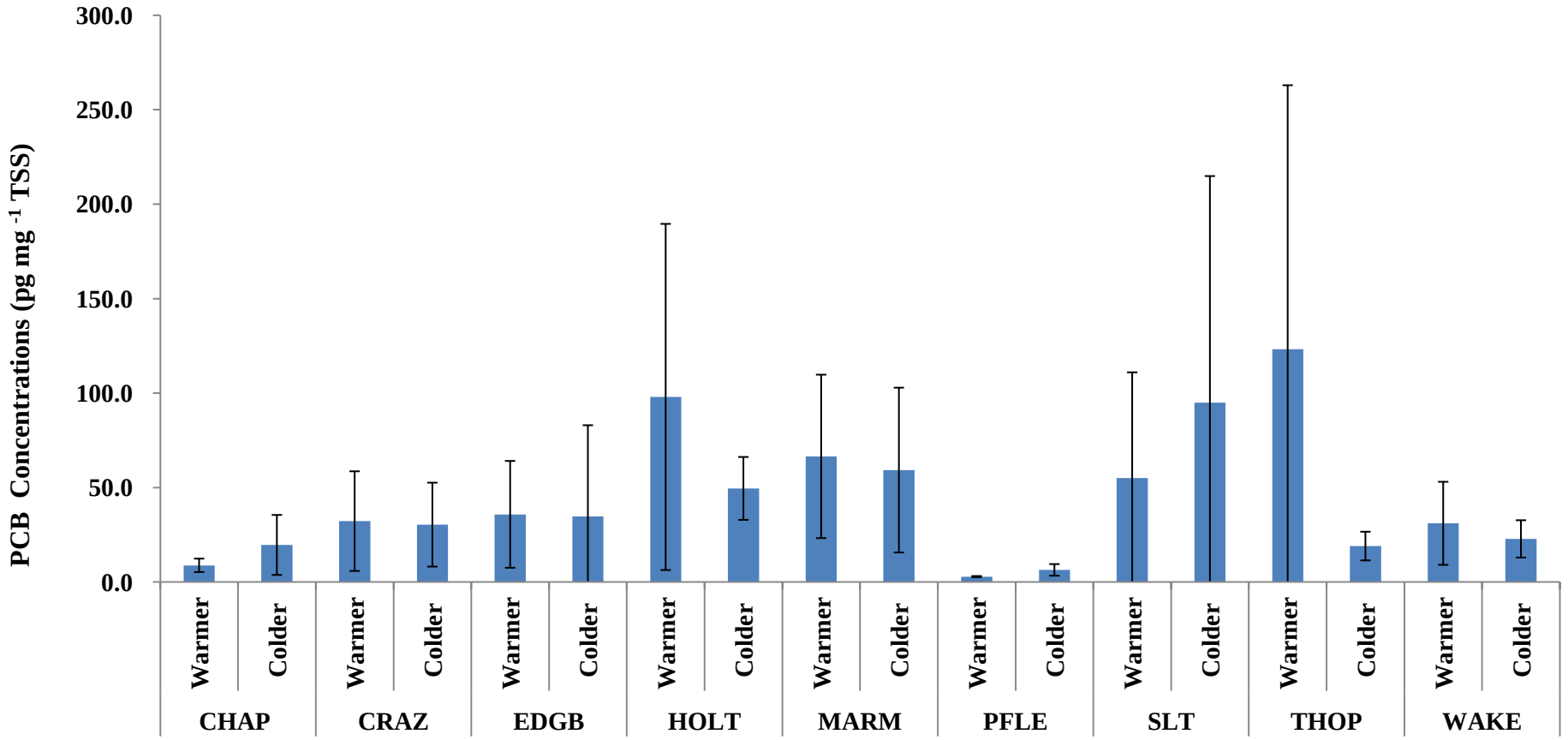


Figure 3.5 Average TSS normalised PCB concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

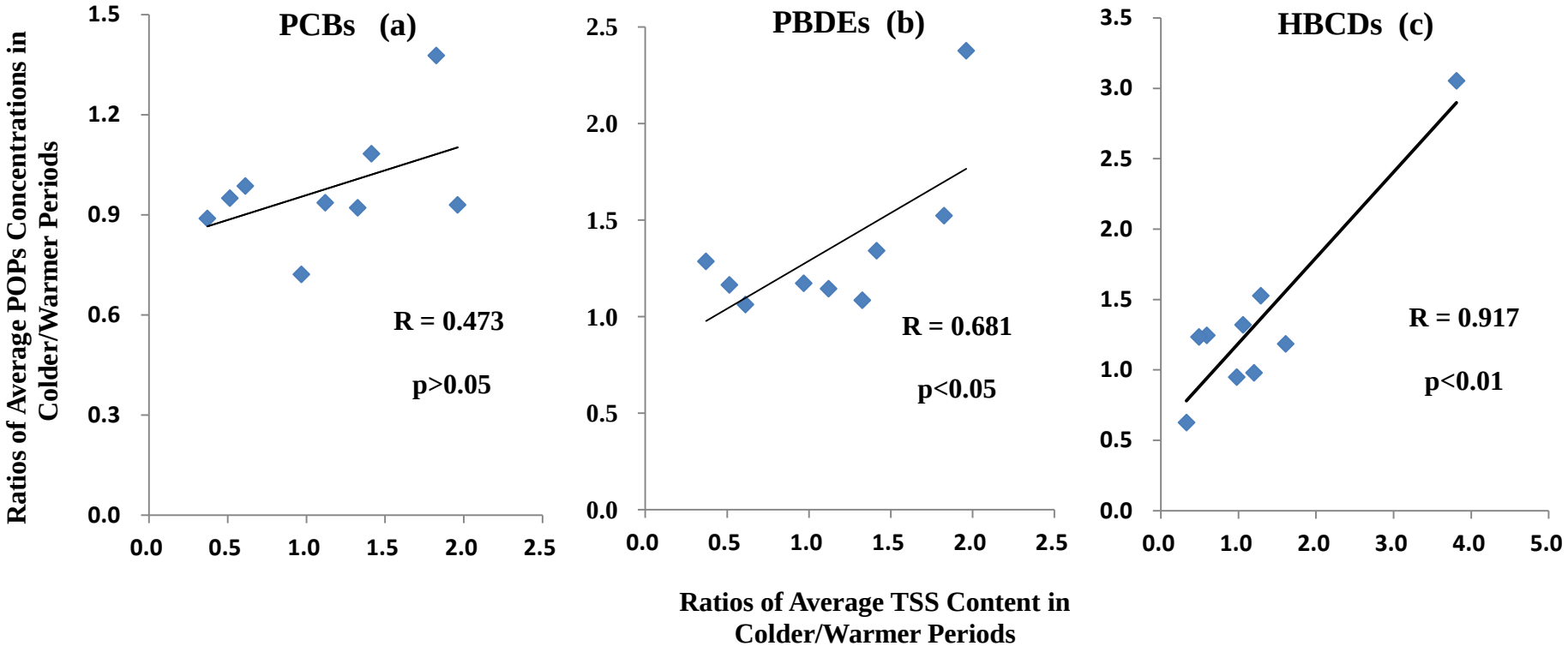


Figure 3.6 Plots of ratios of average TSS content at individual sites in colder/warmer periods against ratios of average concentrations in colder/warmer periods of: (a) ΣPCBs & (b) ΣBDEs (April 2008-February 2012), and (c) ΣHBCDs (July 2008-February 2012)

In addition to seasonal variation in TSS content, we also hypothesise that another likely explanation for our observed winter peak in ΣBDE concentrations at some locations is that lower water temperatures will reduce the extent of PBDE volatilisation. Another possible contributory factor is that the rate of any PBDE degradation will be slower at lower temperatures. Both of these factors favour higher PBDE concentrations when water temperatures are lower.

Multi-linear regression was thus employed to examine the influences of TSS and temperature on PBDE contamination levels. While no significant correlation between the lake water temperature taken at each sampling event and PBDE concentrations was found; inclusion of TSS data along with season (warmer periods were defined as 1; while colder periods were defined as 2) in multi-linear regression analysis revealed significant positive correlations between both parameters and ΣBDEs:

$\Sigma BDEs = 17.844\ season + 0.53\ TSS + 30.893$; $R=0.365$, $p<0.05$; $\beta=0.313$ for season and $\beta=0.222$ for TSS (3.1)

This confirms that ΣBDEs concentrations were higher in colder months and at higher TSS values. The higher β value for season (β=0.313) than for TSS (β=0.222) in equation 3.1, suggests the former to exert a slightly stronger influence on PBDE contamination levels. This suggests that seasonal factors such as reduced volatilisation and degradation in colder periods are also important influences on PBDE concentrations.

Data on PBDE seasonal trends in water bodies with which to compare our data are extremely scarce. Luo et al. (2008) reported that PBDEs in water from the Zhujiang River Estuary displayed some seasonal variation, being lower in May than October. However, in this instance, rather than water temperature or TSS, the seasonal variation was attributed to the fact that in May, brackish water was dominant in the estuary, as opposed to the situation in October when fresh water from river runoff, which was indicated to be the major contributor of PBDEs into the estuary, was dominant.

Seasonal Impacts on concentrations of HBCDs Across the monitored period, HBCDs displayed similar seasonal trends to PBDEs in this study, showing higher average concentrations of ΣHBCDs (expressed on both a water volume and TSS content basis) in colder periods at most (but not all) sites, as shown in Figure 3.9 and 3.10.

Very striking is that, consistent with PBDEs, the ratios of average HBCD concentrations in

colder periods relative to those in warmer periods at each individual site displayed a significant positive linear correlation ($p<0.001$) with seasonal ratios for TSS (Figure 3.6 (c)). This indicates that - as with PBDEs - TSS is an important factor driving ΣHBCD concentrations in English lake water. However, as for PCBs, regression analysis of data for all samples from all sites combined showed no significant positive correlation either between HBCD concentrations and TSS, or a combination of TSS and season or water temperature.

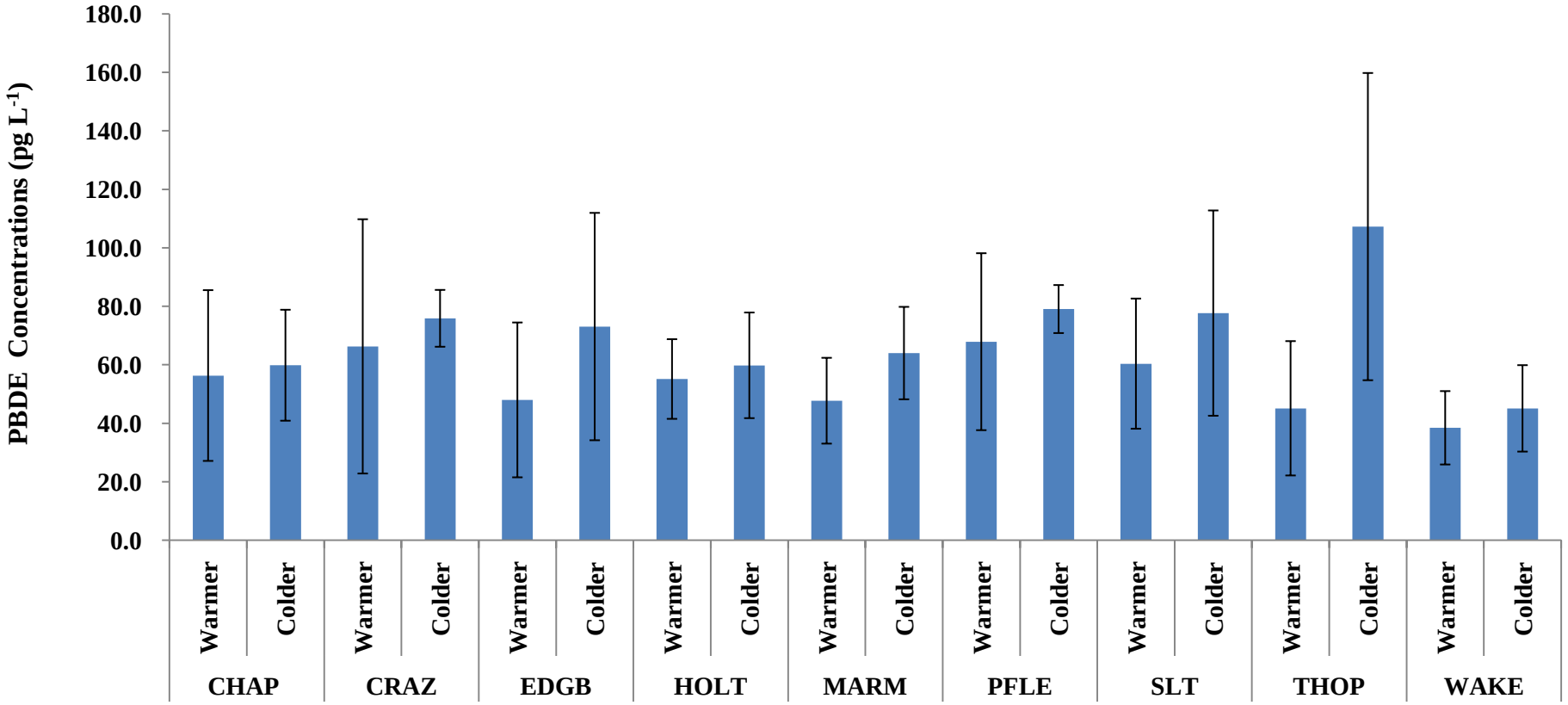


Figure 3.7 Average PBDE concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

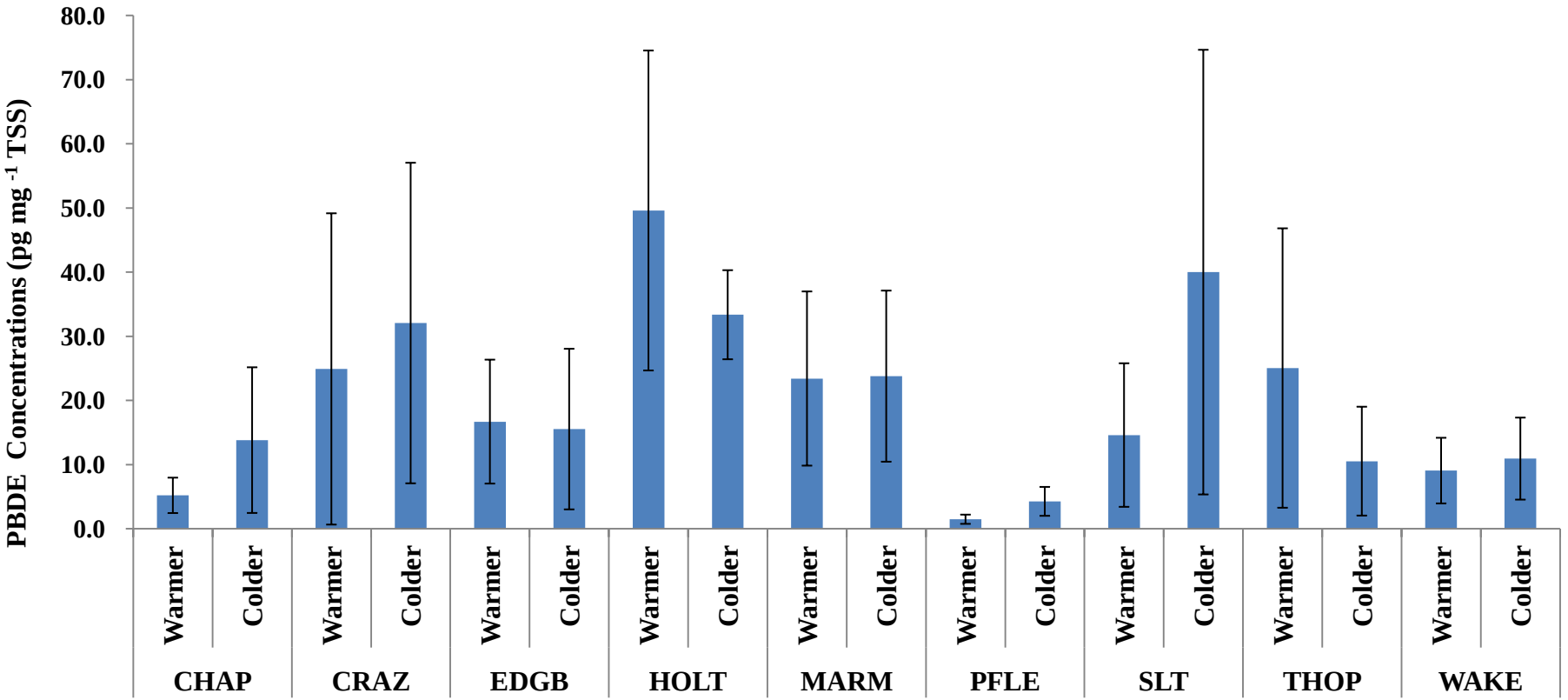


Figure 3.8 Average TSS normalised PBDE concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

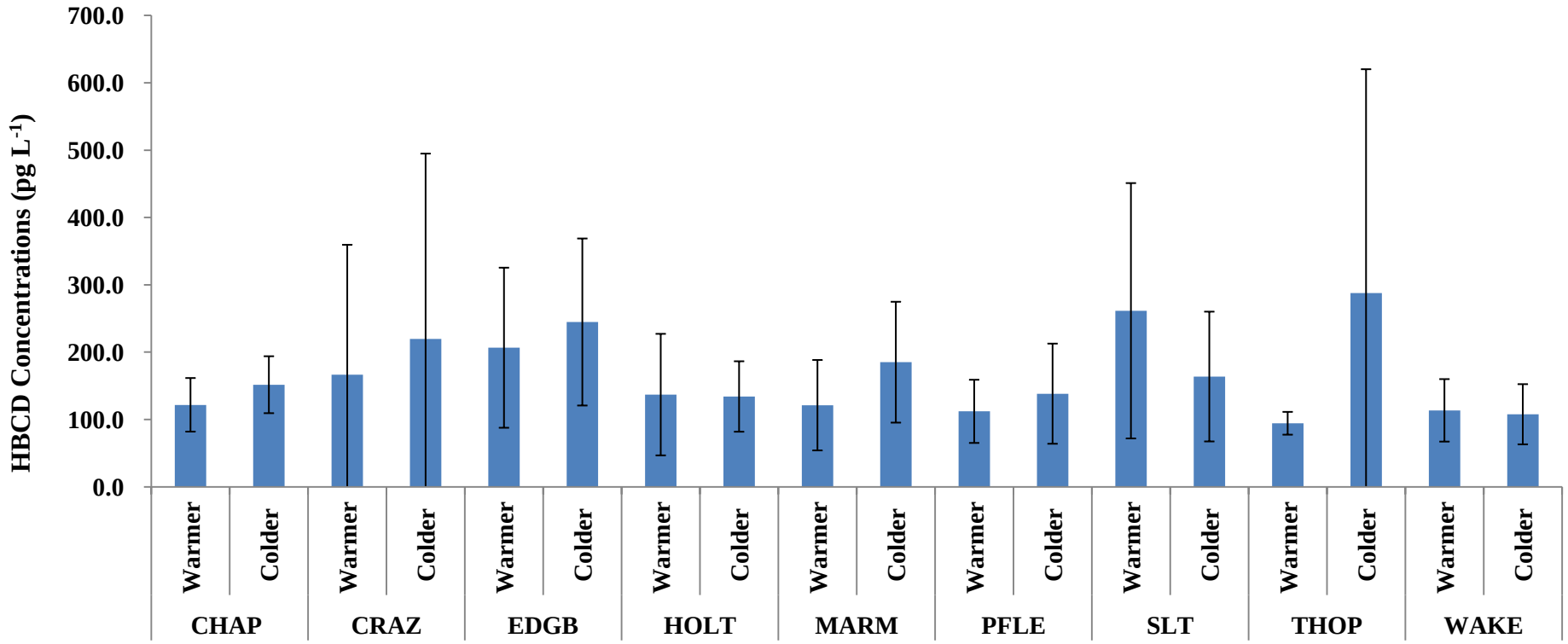


Figure 3.9 Average HBCD concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, July 2008 to February 2012

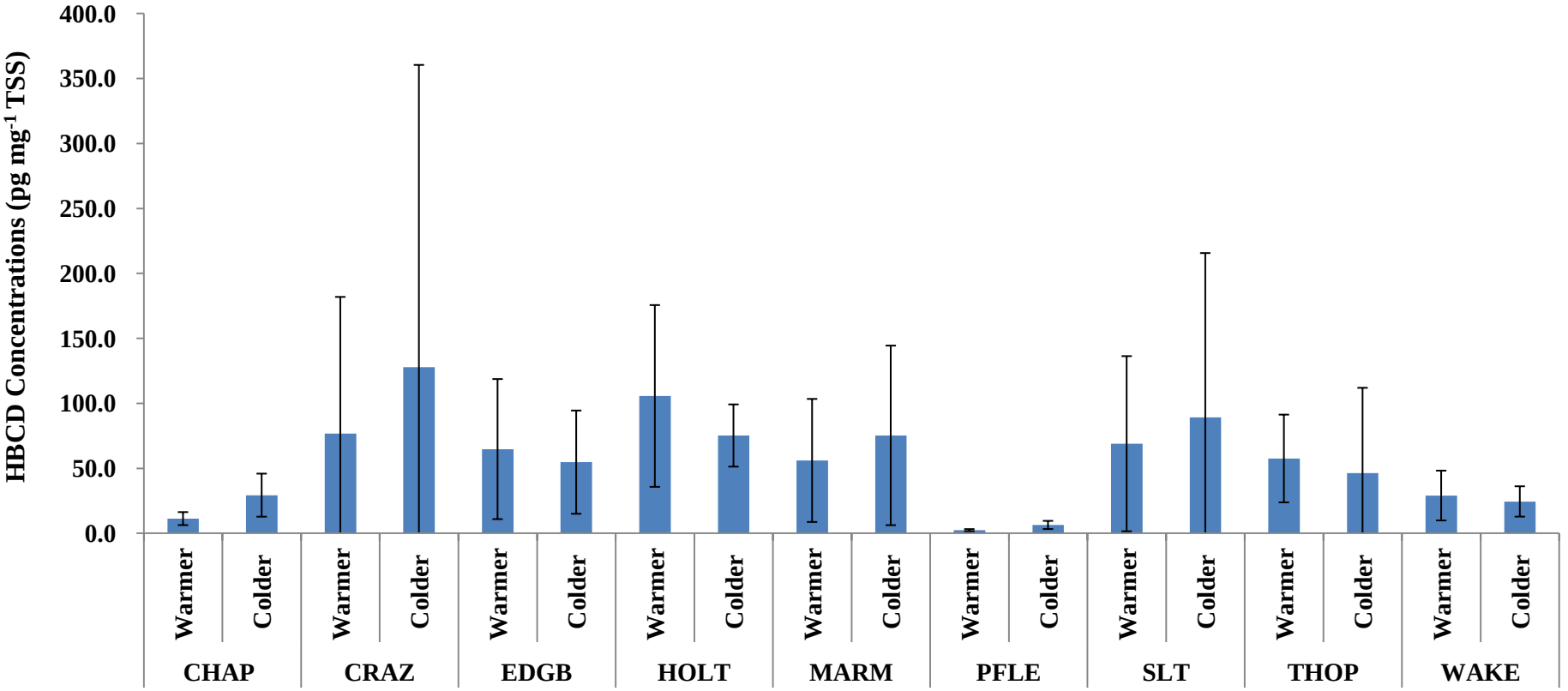


Figure 3.10 Average TSS normalised HBCD concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, July 2008 to February 2012

3.4.3 Temporal Trends in Concentrations of POPs in English Lake Water

Temporal Trends in Concentrations of PCBs Across all samples, linear regression analysis showed statistically significant decreasing trends of ln(PCBs, pg L^{-1}) over the monitored period (R=-0.429, p<0.001). This is illustrated by Figure 3.11, where the first sampling date was defined as day=0 and the last sampling day=1387 for PCBs and PBDEs (1274 for HBCDs owing to the fact that the 1st sample batch was not analysed for HBCDs). The half-life time ($T_{1/2}$) was estimated using the equation:

$T_{1/2}$=1/Slope(k)*ln(2)

Where k = the 1st order rate constant for the decline/increase in POPs concentrations (day^{-1})

The half-life time of ΣPCBs in English lake water was thus estimated to be 3.8 years (1383 days) based on water volume based concentrations.

With respect to individual lakes, though all the nine monitored lakes in this study showed decreasing trends in ln(PCBs, pg L^{-1}) over time, only HOLT (R=-0.623, p=0.012), MARM (R=-0.764, p=0.001), SLT (R=-0.877, p<0.001), and WAKE (R=-0.573, p=0.020) showed statistical significance, with estimated $T_{1/2}$ values of 3.8 (1397 days), 2.4 (870 days), 1.6 (597 days), and 2.9 (1069 days) years, respectively.

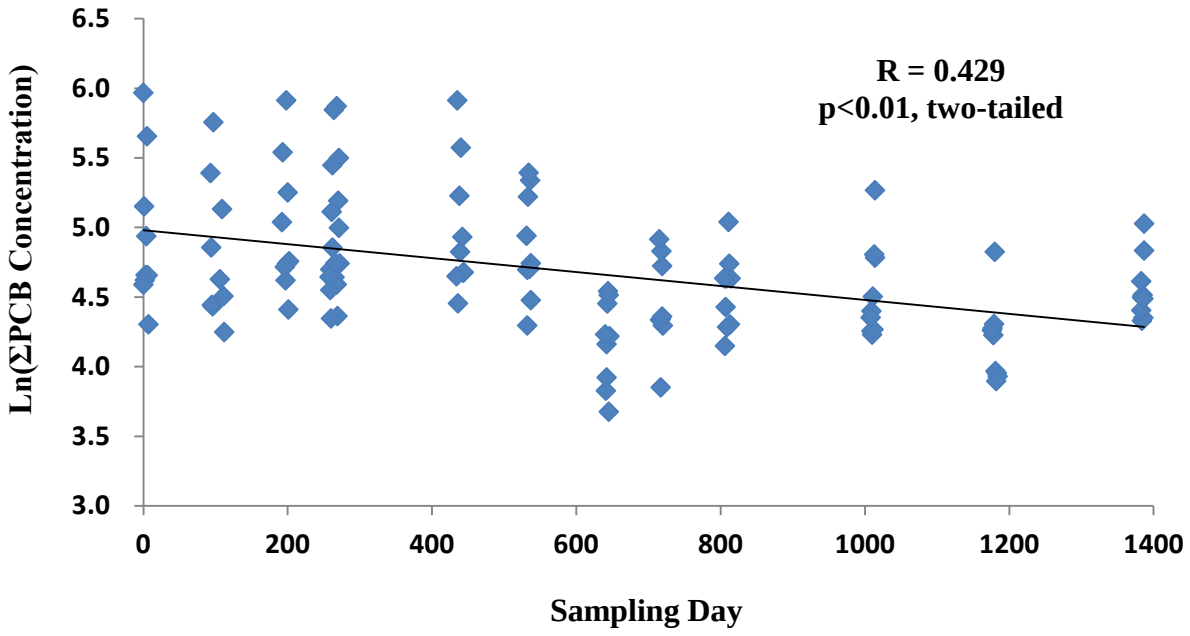


Figure 3.11 Temporal trends in PCB concentrations across all lakes over the monitored period, April 2008-February 2012

To the best of our knowledge, this is the first study of temporal trends in PCB concentrations in water; however, studies of other environmental compartments have revealed generally declining temporal trends over the last 20-30 years. For example, Σtetra-hepta-CBs showed a general decreasing trend over the period 1980-2002 in archived suspended sediment samples at Niagara-on-the-lake in the Niagara river (Marvin et al., 2007). Moreover, in sediment cores from Lake Greifensee, and Lake Thun in Switzerland, concentrations of PCBs have decreased since their 1960s peak (Zennegg et al., 2007; Bogdal et al., 2008). Likewise, sediment core data for the Lake Maggiore basin in Italy and Switzerland shows PCBs to have decreased steadily since 2000 (Guzzella et al., 2008). Schuster et al. (2010) reported a first order decay in atmospheric PCB concentrations ($T_{1/2}$=8.4±3.2 years) over the period 1994-2008 in a study of a rural/remote latitudinal transect from southern UK to northern Norway. Broadly similar findings were reported by Sun et al. (2007) at five out of seven sites in a study of the Great Lakes atmosphere from early/mid 1990s to 2002/3, with a $T_{1/2}$ of PCBs of 7.1-26 years. Interestingly, however, an increasing trend was reported at one site with concentrations remaining essentially stable at the remaining location.

Temporal Trends for PBDEs A statistically significant increasing trend in ln(ΣBDEs, pg L^{-1}) was observed at MARM (R=0.632; p=0.01), with a doubling time (T_2) of 3.3 years (1214 days). Aside of this, there was no evidence of significant temporal trends in ln(ΣBDEs, pg L^{-1}) over the 4 year monitoring period. This is in contrast with recent observations of declining atmospheric concentrations. Specifically, European background airborne PBDE concentrations (BDEs -28, -47, -49, -99, -100, -153, -154, and -183) were reported to have declined with a half-life of 2.2±0.4 years between 2000 and 2008 (Schuster et al., 2010). Likewise, concentrations in air of a similar range of PBDEs were reported to be declining during the 2000s at 3 out of 4 UK monitoring locations with average half-lives between 2.0 and 3.5 years (Birgul et al., 2012). Despite such evidence from the atmosphere of encouraging responses to the recent restrictions on use of PBDEs in the EU; the absence of any decline on concentrations in lake water in our study is not surprising given the four year duration of our study, the lack of any known direct point sources of PBDEs to our lakes, and the comparatively long mixing times of freshwater lakes in general, that exceed those of the atmosphere. It is also possible that any decline in PBDE concentrations at our lakes was rapid following the restrictions on PBDE manufacture and use, and had thus occurred before our study commenced. We also note that no decline in atmospheric PBDE concentrations was observed at one of the two UK rural sites monitored by Birgul et al. (2012). Further

longer-term monitoring is therefore required to elucidate the impact on the lacustrine environment of restrictions on manufacture and use of PBDEs within the EU.

Temporal Trends for HBCDs When data for individual sites are examined, ln(ΣHBCDs, pg L^{-1}) declined significantly at CHAP (R=-0.569, p=0.027; $T_{1/2}$ =1279 days), MARM (R=-0.731, p=0.003; $T_{1/2}$=648 days), and SLT (R=-0.708, p=0.005; $T_{1/2}$ =550 days). Moreover, HBCD concentrations across all sites decreased significantly over the monitoring period (R=-0.24, p=0.006), with a half-life time of approximately 5.1 years (1875 days) (see Figure 3.12). To the best of our knowledge, this is the first report of temporal trends in the concentration of HBCDs in freshwater bodies.

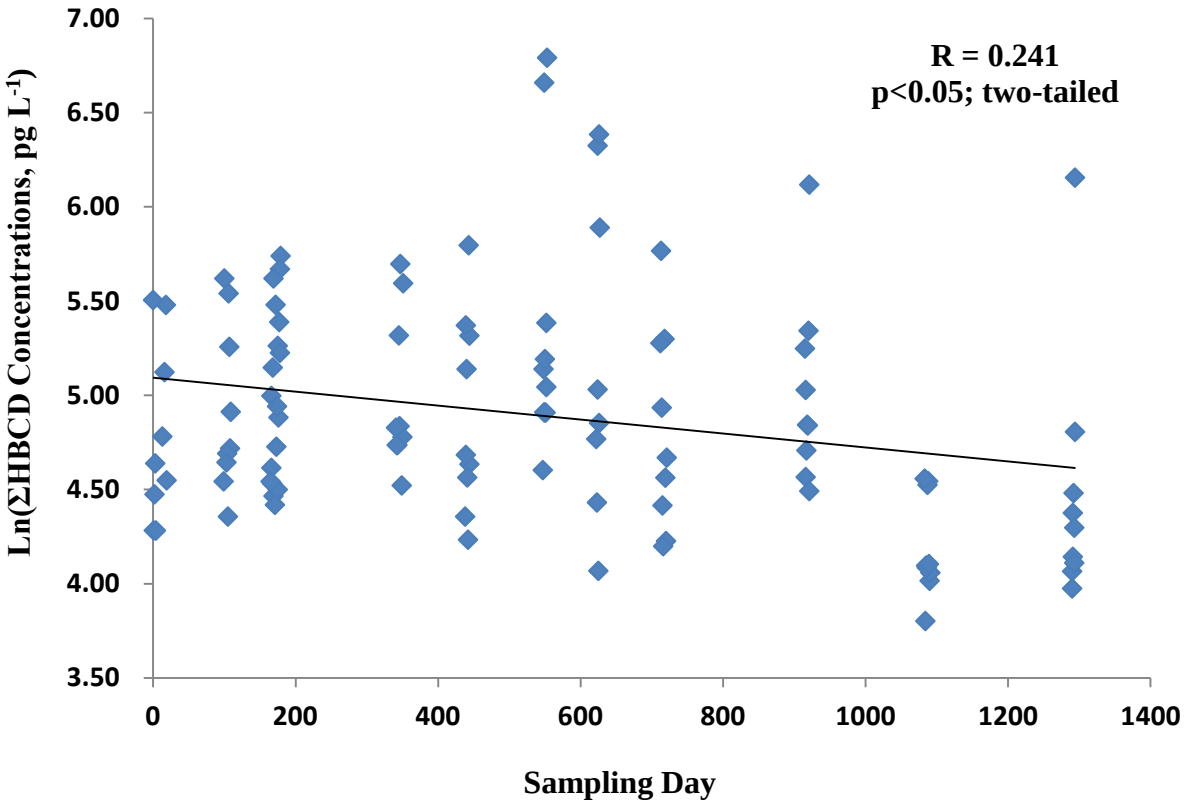


Figure 3.12 Temporal trends of HBCD concentrations over the monitored period, July 2008-February 2012

3.4.4 Spatial Trends in Concentrations of POPs in English Lake Water

In this study, statistically significant inter-site variability was discovered for PCB concentrations expressed on both a water-volume and TSS normalised basis (ANOVA, p<0.01

for both). As shown in Table 3.1, the average water-volume based PCB concentrations were highest at THOP, and lowest at CRAZ; while the highest and lowest PCB concentrations expressed on a TSS normalised basis were observed at HOLT and PFLE, respectively.

While no spatial trends were apparent in PBDE concentrations expressed on a water volume basis; significant inter-site variability was observed when PBDE concentrations were normalised for TSS content (ANOVA, $p<0.01$), with the highest and lowest concentrations at HOLT and PFLE, respectively (see Table 3.3), which is consistent with that observed for PCBs in this study.

With respect to HBCDs, statistically significant inter-site variability was discovered in concentrations normalised for TSS (ANOVA, $p<0.05$), with highest levels seen at CRAZ and HOLT, and the lowest at PFLE (Table 3.5), which is consistent with the observations for PCBs and PBDEs. However, like PBDEs, no spatial variation was observed in water volume based HBCD concentrations.

This suggests that location does influence the POPs concentrations observed in water in our lakes. We investigated possible causes of this spatial variation via multi-linear regression of average concentrations of target compounds at each site against factors such as: lake area, mean depth, lake catchment area, lake catchment ratio (defined as the ratio of lake area to catchment area), lake altitude, and the population density of both: (a) the local authority within which each site was located; and (b) the local authorities within a 25 km radius of each site. No significant relationships were detected. These findings likely reflect the fact that concentrations of PCBs, PBDEs, and HBCDs in water in the lakes in this study are a complex integral of many influential factors.

3.5 Congener Profiles

3.5.1 Congener Profile of PCBs

Monitored PCB congeners in this study showed a distinct and reasonably consistent congener pattern across all samples, with lower chlorinated PCBs dominant in the following general order: 28>52>101>118≈153≈138≈180. In brief, PCB 28 contributed 34-75% (average=52%) of total PCBs, while PCB 52 contributed 11-37% (average=21%). In contrast, PCB 153, 138, and 180 contributed only 1-8%, 0-11%, and 0-6% of ΣPCBs, with average values of 5%, 4%, and 2%, respectively. Comparable with our observations, PCBs 28 and 52 combined, contributed over 67% to nearly 100% of the ΣPCBs detected in the water column of Dianchi

Lake in China, with the relative abundance of individual congeners following the order: PCB 28>52>101≈138≈153≈180 (Wan et al., 2011). Moreover, concentrations of tri- to hepta- PCBs (sum of 20 CB congeners) at eight riverine runoff outlets of the Pearl River Delta accounted for approximately 90% of ΣPCBs (sum of tri- through hepta- congeners), with the congener profile generally following the order of Tri->Tetra->Penta->Hexa->Hepta-CBs (Guan et al., 2009). In summary, our observations are generally consistent with other studies. However, in contrast with our study, a predominance of Penta-CBs (PCB 101 and PCB 118) followed by Hexa-CBs (PCB 153 and PCB 138) were found in the dissolved phase, with PCB 153, 101, 138 dominant in the particulate phase of the water column in the Seine Estuary (tetra- to hepta-PCBs determined; Cailleaud et al., 2007)

3.5.2 Congener Profile of PBDEs

The major congeners detected in all 115 samples were BDE-99 and BDE-47. BDE-99 was the dominant congener at most sites with average BDE-47:99 ratios of 0.91, 0.66, 0.59, 0.92, 0.95 and 0.73 at CRAZ, EDGB, HOLT, PFLE, THOP and WAKE respectively. However, average BDE-47:99 ratios of 1.01, 1.02 and 1.08 were observed at CHAP, MARM and SLT, respectively. The BDE-47:99 ratio in a given matrix is a complex integral of the ratio in the initial source (~0.79-0.96 in Penta-BDE formulations; La Guardia et al., 2006), and the comparative environmental fate of the two congeners following emission. The latter is governed by their physicochemical properties, e.g. one would hypothesise greater partitioning to air and water for the more volatile and water-soluble BDE-47, while BDE-99 would partition preferentially to soil and sediment due to its higher Log K_{OA} and Log K_{OW} (Palm et al., 2002). This is consistent with previous studies reporting BDE-47:99 ratios in soil at 10 UK locations of between 0.51 and 0.88, while in outdoor air collected at the same 10 UK locations, BDE-47:99 ratios varied between 2.95 and 3.62 (Harrad and Hunter, 2006). A paired t-test comparing average BDE-47:99 ratios in water samples for each site over all 13 sampling events with those determined in surficial sediment taken in November 2008 at the same sites (see Table 3.7) showed BDE-47:99 ratios were significantly higher ($p<0.01$) in water (0.75 to 1.33, average=1.09) than in surficial sediment (0.29 to 1.16, average=0.62). We hypothesise that the higher K_{OW} of BDE-99 leads to greater partitioning to surficial sediment than water, and thus lower BDE-47:99 ratios in sediment.

In comparison to our study, BDE-47 dominated in most water samples in San Francisco Bay, followed by BDE-99 (Oros et al., 2005). The higher abundance of BDE-99 in our study

compared to that of Oros et al. may be due to a number of factors. These include: differences in PBDE environmental fate and behaviour between estuarine/marine waters and freshwaters, e.g. higher NaCl concentrations in marine/estuarine water would "salt-out" the more lipophilic BDE-99 to surficial sediment; possible international differences in the congener profile of the Penta-BDE formulation used; varying transfer distances between source and sampling site which may alter the relative abundance of different congeners, and/or greater environmental persistence of BDE-99 relative to BDE-47 following recent restrictions on the manufacture and use of Penta-BDE. This latter hypothesis is plausible given the fact that the Penta-BDE formulation was restricted earlier in Europe than in the USA. Moreover, variations in the TSS content of the samples in different studies may play a role. Further to our observations of the important influence of TSS on PBDE concentrations, we also detected a decrease of BDE-47:99 ratios with increasing TSS content in the February 2011 samples for which TSS measurements were made using the entire 40 L sample, as shown in Figure 3.13. We believe this is a result of the stronger partitioning to suspended sediment of BDE-99 relative to BDE-47, driven by its higher Log K_{OC} and Log K_{OW}. To our knowledge, this is the first report of a relationship between BDE-47:99 ratios and TSS in water samples.

Table 3.7 Average BDE47:99 ratios in water samples across 13 sampling events, and BDE47:99 ratios in surficial sediment sampled in summer 2008

	CHAP	CRAZ	EDGB	HOLT	MARM	PFLE	SLT	THOP	WAKE
Water	1.16	1.06	1.13	0.75	1.08	1.03	1.33	1.33	0.92
Surficial sediment	0.85	1.12	0.46	0.39	1.00	0.45	0.43	0.26	0.65

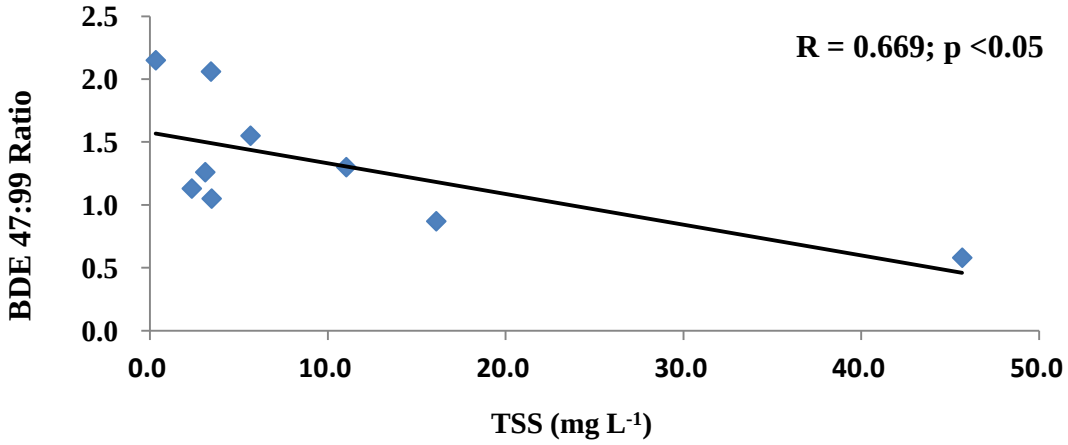


Figure 3.13 Correlations between TSS content (measured for February 2011 samples only) and BDE-47:99 ratio

We also detected that at 7 out of the 9 sampling sites, BDE-47:99 ratios displayed seasonal fluctuation with generally higher ratios observed in samples taken in warmer periods than in colder periods. This was further confirmed by the fact that the BDE-47:99 ratios across all sites were significantly higher in warmer than colder periods (paired sample t-test, $p<0.01$). To our knowledge, this is the first report of such seasonal variation in congener patterns of PBDEs in freshwater lakes. Overall, the average BDE-47:99 ratio in warmer periods exceeded that in colder periods by a factor of 1.48 across 13 sampling occasions. We examined the influence of season on our BDE-47:99 ratios further using linear regression, again defining warmer periods as 1 and colder periods as 2. Defined thus, season showed a statistically significant negative linear relationship with BDE-47:99 ratios across all 115 water samples.

BDE-47:99 = -0.414 season + 1.689; ($R=0.279$, $p<0.01$) (3.2)

In addition, BDE-47:99 ratios across all samples showed significant dependence on water temperature measured 50 cm below the surface at the time of each sampling event as per equation 3.3.

BDE-47:99 = 0.032 temperature + 0.711; ($R=0.261$, $p<0.01$) (3.3)

Interestingly, when each site is examined individually, this seasonal trend in BDE 47:99 ratios was not significant in the first two years of monitoring, but was highly significant in the second half of the monitoring period. Longer term monitoring is required to determine whether seasonal variations in congener profiles are genuine. However, this seasonal variation is consistent with the abovementioned inverse relationship between TSS and BDE-47:99 ratios and our observation of higher TSS in colder periods. Additionally, we suggest that higher BDE-47:99 ratios in warmer than in colder periods may also be due to the fact that in warmer periods one would expect preferential degassing from sediment of the more volatile BDE-47, and enhanced temperature-driven partitioning of BDE-99 to sediment organic carbon in winter.

3.5.3 Congener Profile of HBCDs

Information on HBCD diastereomer patterns in English freshwater lakes in this study is summarised in Figure 3.14. The proportions (average$\pm\sigma_{n-1}$) of α-HBCD and γ-HBCD across all samples ranged from 10 to 43% (28±8%), and 35 to 86% (56±12%), respectively. Regarding each site, the intra-site average percentage contribution ranged from 24 to 35% for α-HBCD, and 46 to 61% for γ-HBCD. The only two relative studies for comparison we are

aware of are: (a) in a study on freshwater (n=5) and seawater (n=5) from Denmark, α-HBCD was the main isomer in most samples, constituting 40-60% ΣHBCDs; however, α-HBCD was below detection limit in 2 samples, meaning overall that both α- and γ-HBCD accounted for 44% of ΣHBCDs (Vorkamp et al., 2014); and (b) while γ-HBCD was detected in 2 out of 12 water samples collected in 2010 from Taihu Lake, α-, and β-HBCD were not detectable (Xu et al., 2013).

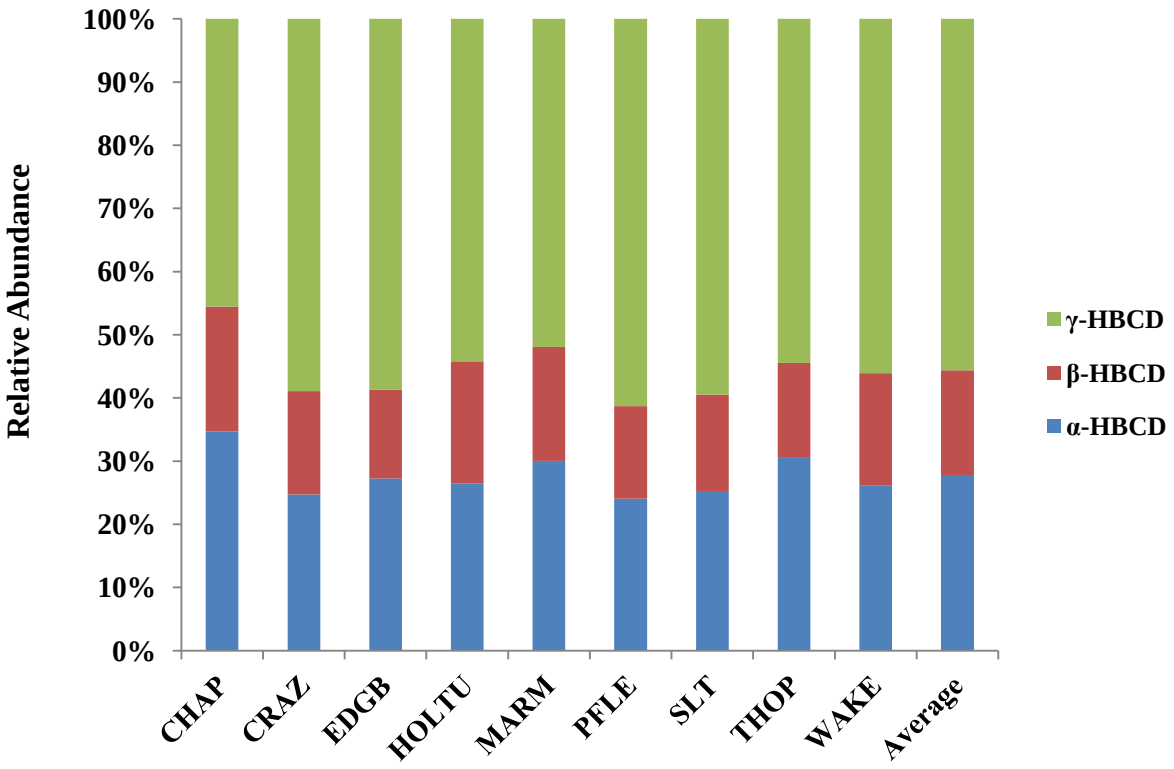


Figure 3.14 HBCD diastereomer pattern (expressed as an average percentage of ΣHBCDs) in individual English freshwater lakes

For comparison, γ-HBCD dominates in HBCD commercial mixtures with a reported percentage contribution of γ-HBCD 75-89%, with α- and β-HBCD present in considerably lower proportions (10-13% and 1-12%, respectively) (Heeb et al., 2005). Clearly, the percentage contribution of γ-HBCD in lake water in the current study is lower than in commercial mixtures. Consistent with this, the average α- and γ-HBCD percentage contributions in indoor air (n=25) were 22%, and 66%, respectively, while for matched indoor dust samples, the average contribution of α-HBCD increased significantly to 33%, with that for γ-HBCD decreasing to 56% (Abdallah, 2009). Moreover, proportions of γ-HBCD in water

samples were statistically significantly lower/higher (paired sample t-test, $p<0.001$ for both) than in paired surficial sediments/fish samples from the same study reported previously (Harrad et al., 2009).

HBCDs have been identified as susceptible to isomerisation at 190℃, with a final composition of 78% α-, 13% β-, and 9% γ-HBCD, regardless of the original composition of the three diastereomers (Peled et al., 1995). As the processes via which HBCDs are incorporated into many applications may involve heat (e.g. adding to molten polymers), this provides a plausible explanation of the higher proportions of α-HBCD observed in water samples in this study. Furthermore, it was also reported that β- and γ-HBCD are degraded more rapidly than α-HBCD under anaerobic conditions (Gerecke et al., 2006).

Very striking is that the percentage contribution of γ- to ΣHBCDs displayed a significantly positive correlation with ΣHBCD concentration expressed on both a water-volume ($r=0.316$, $p<0.01$) and TSS normalised basis ($r=0.237$, $p<0.001$). A plausible explanation for this observation is that higher ΣHBCD concentrations are associated with enhanced fresh "unweathered" inputs of HBCDs, which contain higher proportions of γ- HBCD.

Temporal changes in HBCD diastereomer patterns at each site over the period of this study were insignificant, indicated by the generally low intra-site standard deviations for the proportions of each diastereomer.

Seasonal trends in the relative proportions of α-, β-, and γ-HBCD were also investigated for all sites. No statistically significant variations were found, supported by both the lack of correlations ($p>0.05$) between the proportions of individual diastereomers and temperature; coupled with similar diastereomer profiles in warmer and colder periods ($p>0.05$ via t-test).

Chapter Ⅳ

Temporal Trends of PCBs, "Legacy" and "Novel" BFRs in Radiometrically Dated Sediment Cores from English Lakes, ~1950-2011/2

4.1 Introduction

POPs are of great concern due to their historically abundant production and usage, elevated concentrations in various environmental compartments, commercial products, foods, organisms, and human tissues, and either verified or potential toxicity. In this chapter, both "classic" or "legacy" POPs like PCBs and a wide range of both "legacy" and "novel" BFRs are studied.

Seven lakes are studied from throughout England, possessing various features and representing a mix of urban and rural sites. Seven sediment cores were collected in 2011/2 (one from each lake), covering sedimentation from ~1950 to the present. Monitoring of POPs in lake sediment cores can: 1) enhance understanding of the temporal and spatial trends of these compounds in the environment; 2) permit assessment of differences in the environmental behaviour of different POPs; 3) assist with calculation of environmental burdens of POPs; and 4) facilitate evaluation of environmental responses to bans and/or control measures applied to certain POPs, including increases in use of some compounds as a result of restrictions on others.

4.2 Experimental Section

Details of sampling locations and strategies, sample preparation, analytical methods, instrumental analysis, and QA/QC are described in the methodology chapter (Chapter Ⅱ).

4.3 Temporal Trends of POPs in English Freshwater Lakes over the Last 60 Years

4.3.1 Distribution and Discussion by Compound Group

Concentrations of PCBs, HBCDs, tri- through deca-BDEs, and selected NBFRs were measured in radiometrically-dated sediment core slices taken from seven English freshwater lakes from a

mix of urban, rural, and remote locations in summer 2011/2 (see Table 4.1 for details). Table 4.2 shows the concentrations of target POPs in each sample analysed from the most rural and least contaminated site (CRAZ), as well as the most urban and also most contaminated site (EDGB) in this study. Data for the other 5 sites are summarised in Appendix A (Table 1). These concentration data were used to examine temporal trends in benthic inputs from ~1950 to the present day, with a time resolution of approximately five years. Historical changes in POPs concentrations at all seven English freshwater lakes are illustrated in Figure 1 in Appendix B, with those at the three most contaminated sites EDGB, MARM, and PFLE used as illustrative examples of temporal trends in Figure 4.1. The occurrence of our target POPs in English freshwater sediments appear driven by anthropogenic activities, since concentrations were consistently higher at EDGB, MARM, and PFLE, compared to rural/remote locations like CRAZ and SLT.

Table 4.1 Information on the English freshwater lakes from which sediment cores were taken

Location	Altitude (m)	Mean Depth (m)	Lake Area (m^2)	Catchment Area (km^2)	Catchment Ratio [a]	Average Sedimentation Rate [b] ($g\ cm^{-2}\ y^{-1}$)	Average Sedimentation Rate [b] ($cm\ y^{-1}$)	Population density [c]	Population density [d]
CRAZ	244	1	101,000	1.8	0.05	0.046	0.318	≤99	≤99
EDGB	127	0.9	72,000	6.4	0.01	0.054	0.469	>2500	>2500
HOLT	47	0.6	7,000	0.6	0.01	0.097	1.147	100-249	100-249
MARM	7	1.35	108,000	10.2	0.01	0.232	0.881	>2500	>2500
PFLE	68	0.5	264,000	12.3	0.02	0.061	0.349	250-499	>2500
SLT	3	-	659,000	17.7	0.03	0.050	0.524	≤99	1000-2499
WAKE	96	1.7	10,000	0.3	0.03	0.121	0.772	250-499	>10000

[a] Lake catchment ratio was defined as the ratio of lake area to lake catchment area

[b] Average sedimentation ratios were the mean values of sedimentation ratios for each segment, calculated using ^{210}Pb radiometric dating results

[c] Population density (people per sq km) of local/unitary authority of lake site

[d] Population density (people per sq km) of local/unitary authorities within 25km of site

Table 4.2 Part 1: Concentrations[a] of "legacy" and "novel" BFRs (ng g^{-1} TOC) in sediment core segments from CRAZ

Concentrations at CRAZ									
Compound \ Average Year	2009	2004	1998	1991	1983	1977	1972	1963	1955
ΣPCBs[b]	7.08	6.79	8.41	12.2	15.3	17.9	20.3	21.9	17.5
ΣHBCDs[c]	4.33	28.9	1.83	2.01	0.34	0.49	0.16	0.13	0.11
Σtri-hexa-BDEs[d]	2.11	2.61	3.34	1.44	1.02	1.15	0.20	<0.01	<0.01
BDE-183	0.24	0.13	0.07	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
BDE-209	4.39	4.80	3.25	1.78	2.15	0.57	0.44	0.93	<0.13
TBPH	8.95	4.99	6.88	5.67	1.68	<0.84	<0.84	<0.84	<0.84
PBEB	2.05	1.87	13.6	1.50	1.98	1.90	2.53	2.09	3.42
TBB	0.56	0.64	0.54	0.52	0.36	0.37	0.23	<0.03	<0.03
TBBPA-DBPE	3.98	3.78	1.25	1.55	0.97	<0.79	<0.79	<0.79	<0.79
BTBPE	0.79	0.64	0.07	0.33	0.12	0.05	0.03	<0.01	<0.01
DBDPE	1.27	0.70	0.29	0.39	<0.18	<0.18	<0.18	<0.18	<0.18
HCDBCO	0.39	0.51	0.26	0.33	0.68	0.57	0.36	0.58	0.54
TBECH	0.33	0.23	0.19	0.27	0.26	0.22	0.17	0.18	0.25
HBB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBCC	2.12	0.85	0.09	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBBB	0.69	0.78	0.50	0.22	<0.11	<0.11	<0.11	<0.11	<0.11
sDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
aDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ΣDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Limit of quantification (LOQ, ng g^{-1} TOC) was reported where compound was found below detection limits

[b] sum of PCB-28, -52, -101, -118, -153, -138, -180; [c] sum of α-, β-, and γ-HBCD isomers; [d] sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153

Table 4.2 Part 2: Concentrations[a] of "legacy" and "novel" BFRs (ng g^{-1} TOC) in sediment core segments from EDGB

Concentrations at EDGB											
Average Year / Compound	2008	2003	1998	1992	1987	1982	1977	1970	1965	1960	1956
ΣPCBs [b]	74.0	150	219	278	326	469	388	365	403	140	200
ΣHBCDs [c]	23.9	19.3	16.2	11.3	10.4	6.34	5.32	6.26	2.21	<0.005	<0.005
Σtri-hexa-BDEs [d]	14.1	6.15	6.32	4.53	5.54	3.94	2.77	1.61	<0.03	<0.03	<0.03
BDE 183	5.45	2.87	4.40	6.09	6.72	7.33	4.62	1.43	<0.04	<0.04	<0.04
BDE 209	351	251	207	135	120	98.0	89.5	53.1	41.5	13.3	19.6
TBPH	609	515	443	876	107	113	58.2	27.7	<0.84	<0.84	<0.84
PBEB	39.8	35.9	26.4	12.2	7.98	36.5	13.6	1.37	<0.02	<0.02	<0.02
TBB	22.4	16.9	11.6	23.1	9.17	5.90	<0.03	<0.03	<0.03	<0.03	<0.03
TBBPA-DBPE	15.7	18.3	9.46	20.9	14.0	16.2	3.02	3.44	<0.79	<0.79	<0.79
BTBPE	5.38	1.67	3.34	1.41	1.49	1.52	0.66	<0.01	<0.01	<0.01	<0.01
DBDPE	6.35	5.63	3.28	2.20	1.71	1.72	<0.01	<0.18	<0.18	<0.18	<0.18
HCDBCO	9.03	9.28	6.00	3.25	3.75	2.67	2.77	1.95	2.55	<0.03	<0.03
TBECH	2.91	2.62	2.24	1.89	1.38	0.96	<0.03	<0.03	<0.03	<0.03	<0.03
HBBb	0.72	0.59	0.58	0.34	0.36	0.09	0.13	<0.01	<0.01	<0.01	<0.01
PBCC	4.39	4.27	2.28	1.52	1.84	0.97	0.55	<0.01	<0.01	<0.01	<0.01
PBBB	0.32	0.30	0.36	0.22	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
sDP	1.21	1.18	0.82	0.77	0.16	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
aDP	0.39	0.60	0.16	0.44	0.45	0.12	<0.01	<0.01	<0.01	<0.01	<0.01
ΣDP	1.60	1.78	0.98	1.21	0.62	0.12	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Limit of Quantification (LOQ, ng g^{-1} TOC) was reported where compound was found below detection limits

[b] sum of PCB-28, -52, -101, -118, -153, -138, -180; [c] sum of α-, β-, and γ-HBCD isomers; [d] sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153

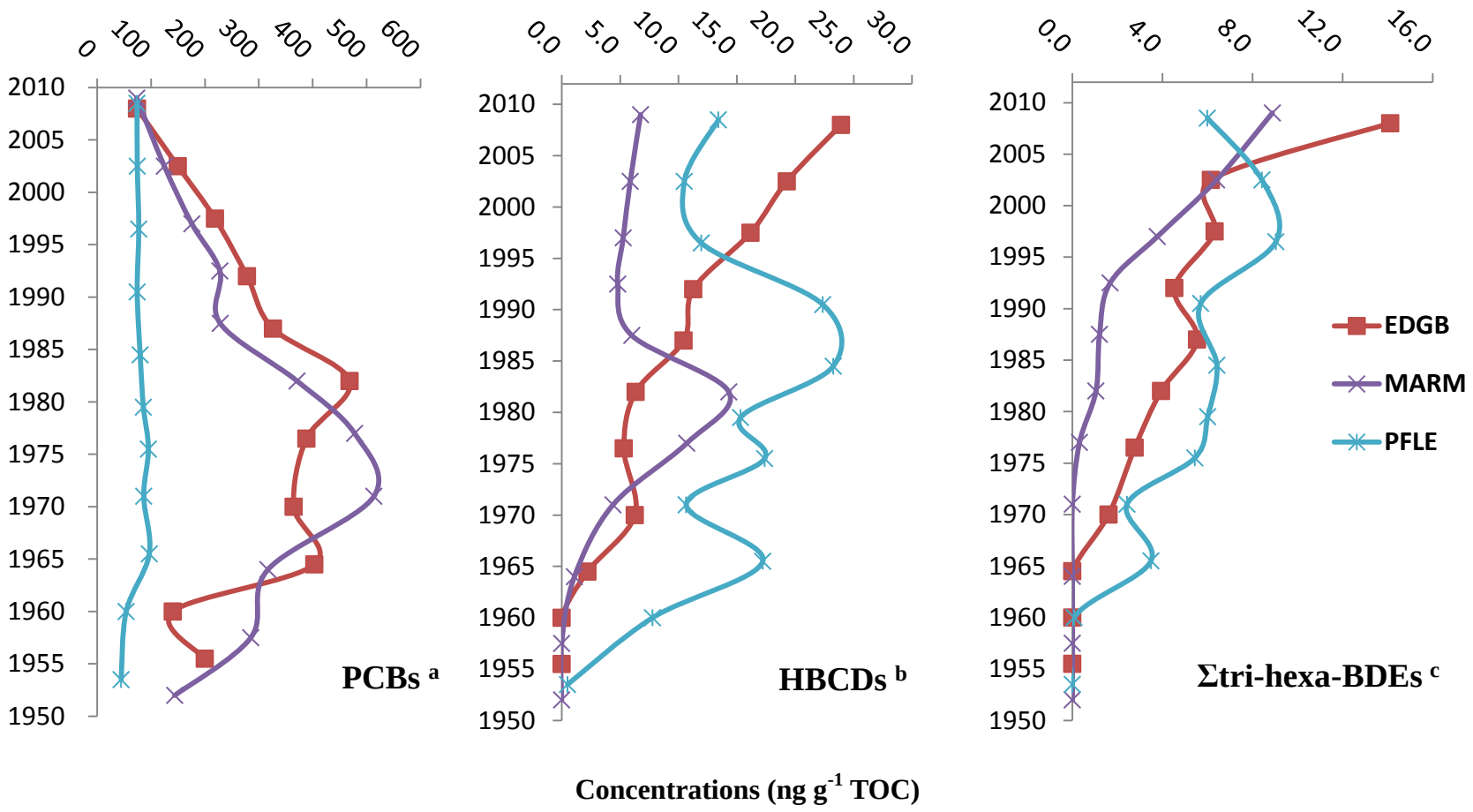


Figure 4.1 Part 1: Temporal trends of concentrations (ng g^{-1} TOC; x axis) of PCBs, HBCDs, and Σtri-hexa-BDEs in sediments from the three most contaminated English freshwater lakes in this study, ~1950-2011/2; average year of sedimentation for each core slice plotted as the date

[a] sum of PCB-28, -52, -101, -118, -153, -138, -180; [b] sum of α-, β-, and γ-HBCD isomers; [c] sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153.

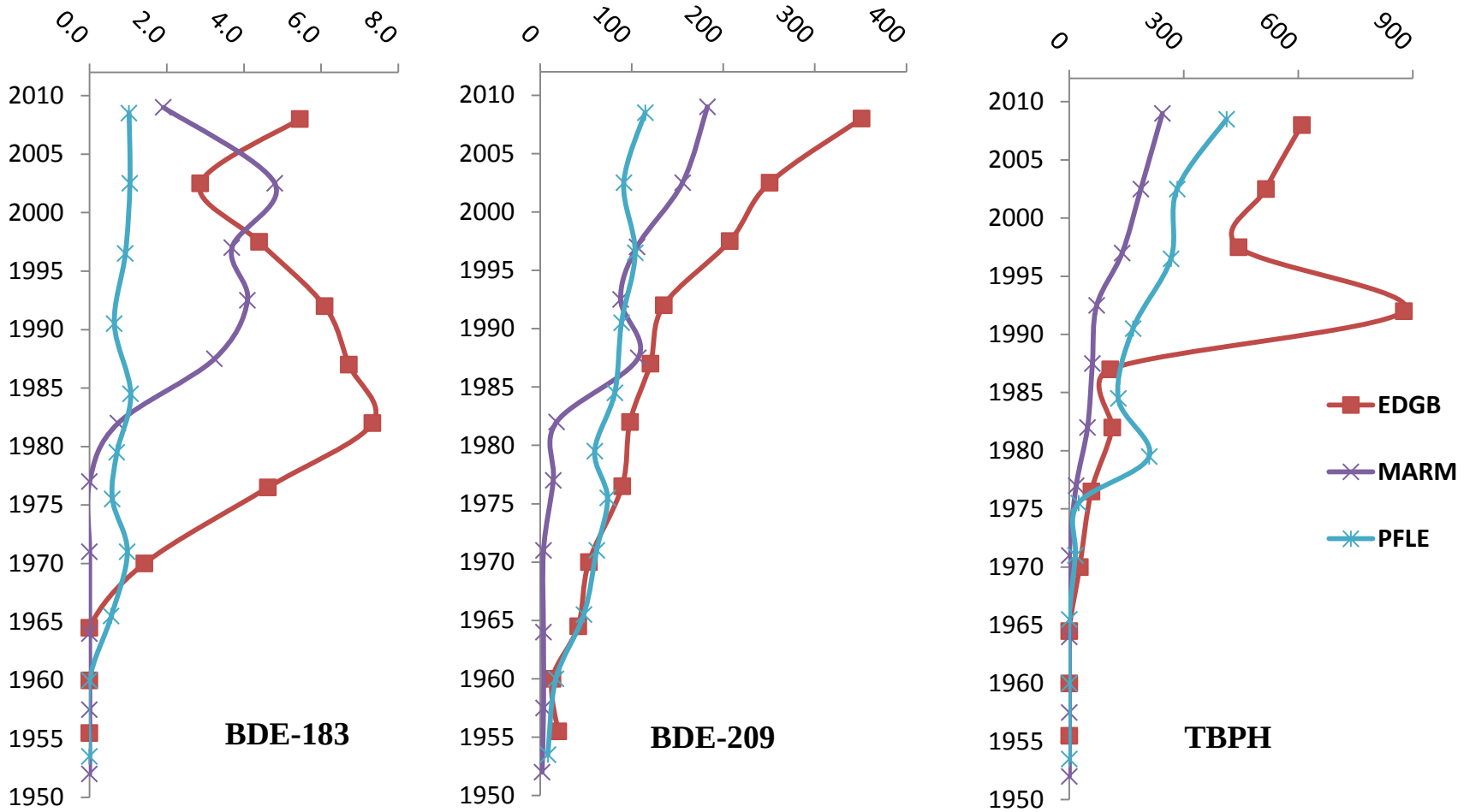


Figure 4.1 Part 2: Temporal trends of concentrations (ng g^{-1} TOC; x axis) of BDE-183, BDE-209, and TBPH in sediments from the three most contaminated English freshwater lakes in this study, ~1950-2011/2; average year of sedimentation for each core slice plotted as the date

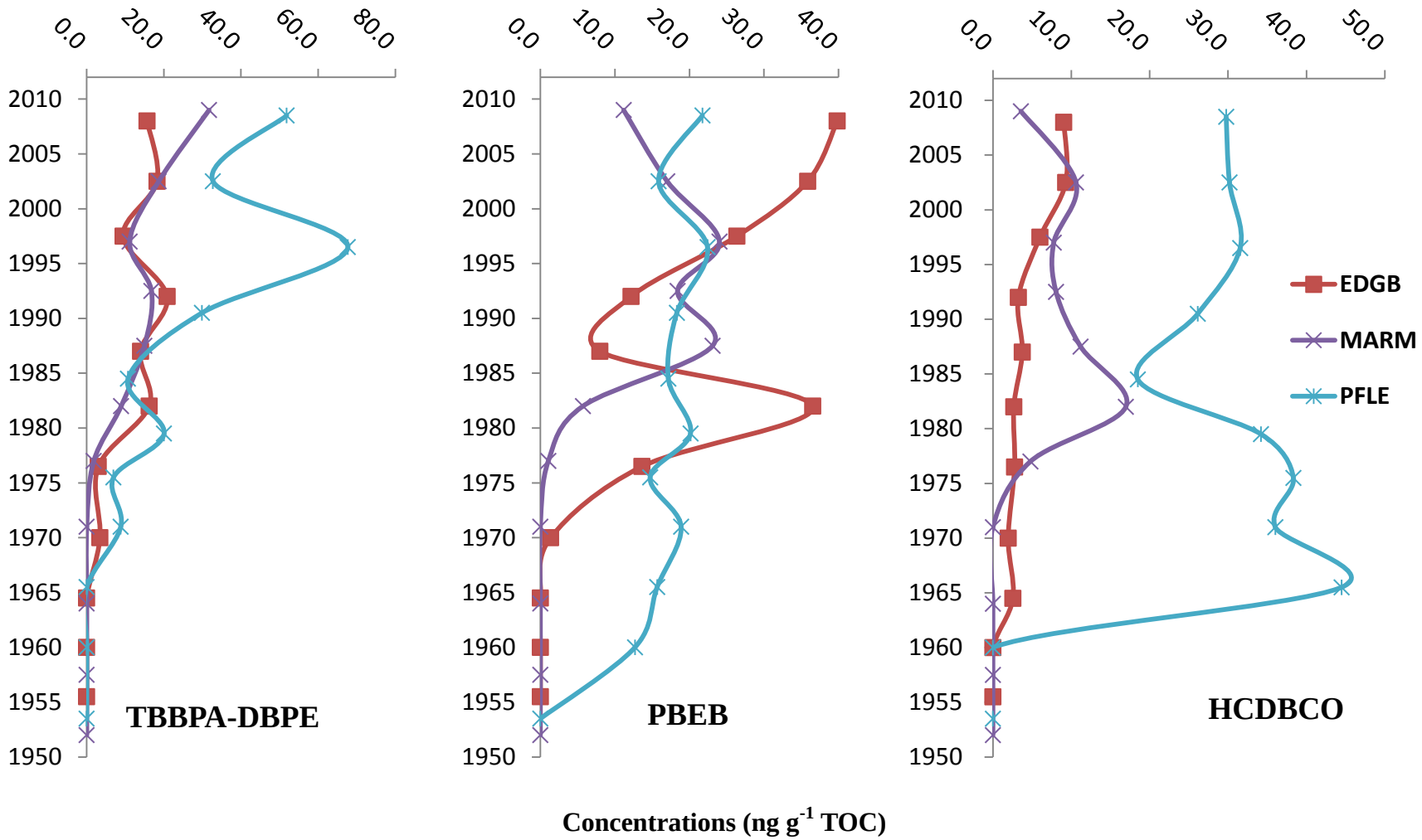


Figure 4.1 Part 3: Temporal trends of concentrations (ng g^{-1} TOC; x axis) of TBBPA-DBPE, PBEB, and HCDBCO in sediments from the three most contaminated English freshwater lakes in this study, ~1950-2011/2; average year of sedimentation for each core slice plotted as the date

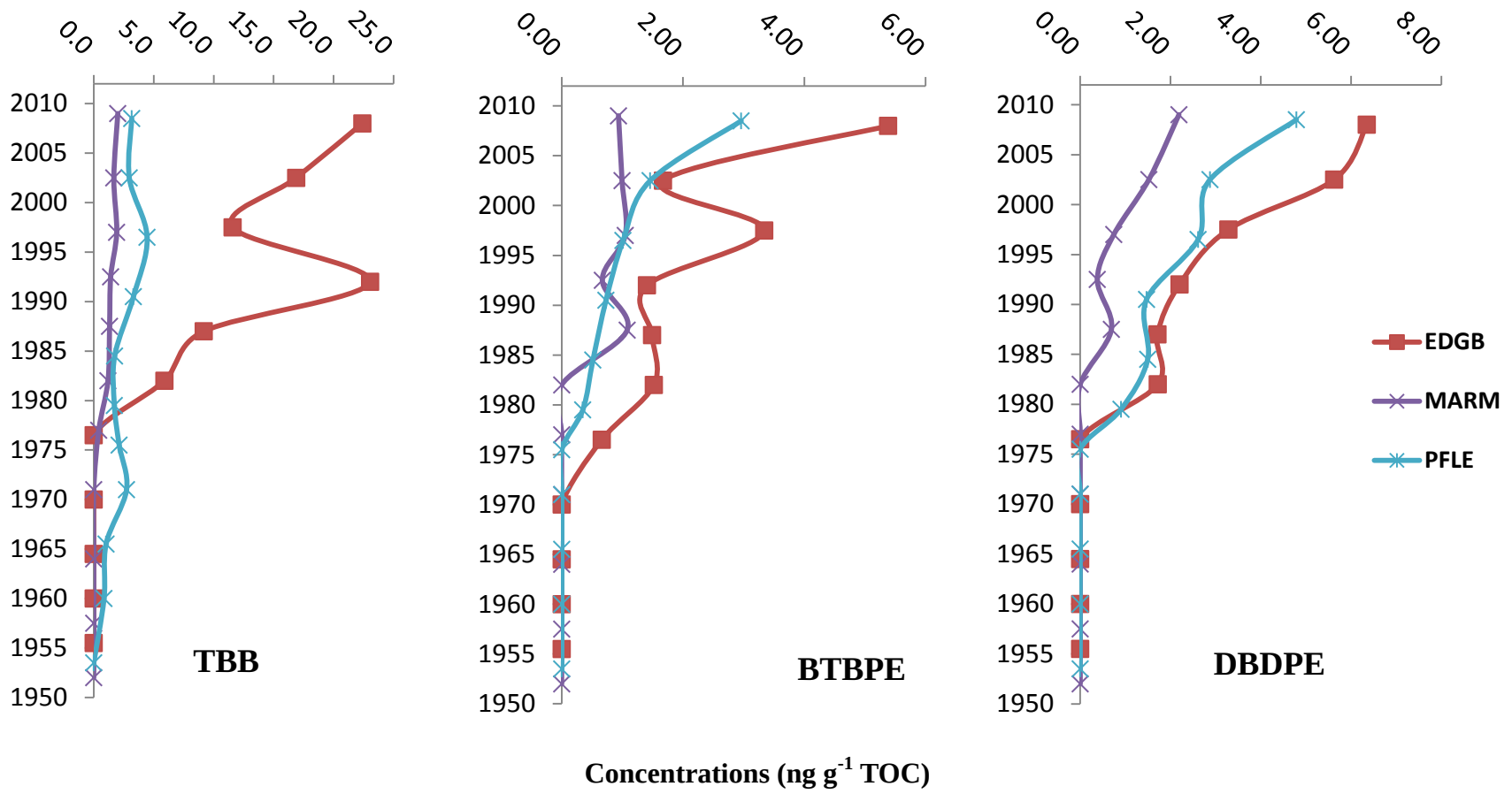


Figure 4.1 Part 4: Temporal trends of concentrations (ng g^{-1} TOC; x axis) of TBB, BTBPE, and DBDPE in sediments from the three most contaminated English freshwater lakes in this study, ~1950-2011/2; average year of sedimentation for each core slice plotted as the date

4.3.1.1 PCBs

The inclusion of PCBs in this study had two main purposes: 1) to gain a comprehensive understanding of their spatial and temporal trends in England; and 2) to provide a further "tool" (over and above the radiometric dating) for dating the sediment core slices. This is because in contrast to the BFRs monitored here, temporal trends of PCBs in the UK environment are comparatively well-characterised (Gevao et al., 1997; Sanders et al., 1992; Rose and Rippey, 2002). Our data show that PCB contamination at all lakes in this study increases from the lowest depth slices dated to ~1950, peaking generally between the late-1960s and mid-1980s, before declining steadily thereafter. That these temporal trends accord with previous UK studies, and historical trends in UK manufacture and use, adds weight to the accuracy of the dates assigned to core slices via radiometric dating.

The modest variation in the timing of peak concentrations between sites in this study is consistent with the findings of Sanders et al. (1992) and Gevao et al. (1997). These earlier studies reported different PCB maximum loading dates (1953-1963 and 1979±2, respectively) for the same UK lake (Esthwaite Water). Intra-lake variations in sedimentation ratios, combined with possible different methods of generating subsamples, were proffered as possible explanations for the difference between the two studies (Gevao et al., 1997). In a remote lake in north-west Scotland, maximum PCB concentrations were observed in 1965-1979 following a gradual increase before this period, with a decrease observed in the top layer representing the year up to 1996 (Rose and Rippey, 2002).

Outside the UK, similar studies of historical inputs of PCBs to sediments display variable emerging and peaking times for PCB contamination, but there is a consistent pattern that PCBs have increased rapidly following their emergence in the environment following the onset of their manufacture (1930 in USA and Germany, later - i.e. 1954 in the UK with up to 100 t imported prior to this date), peaked somewhere between the mid-1960s and mid-1980s, before declining with variable degrees of rapidity. Broadly consistent with our observations, a study on the Swiss Lake Greifensee showed PCBs made their first appearance in sediment core slices as early as 1940, increased rapidly to a peak around 1960 before decreasing rapidly until around 1980, followed by a more gentle decrease/levelling off thereafter (Zennegg et al., 2007). Also in Switzerland, PCBs peaked in 1961 and 1965, respectively, and decreased rapidly and consistently

thereafter in two of the three sediment cores from Lake Thun, while in the third core, concentrations remained relatively low and peaked at around 1990. PCBs first appeared in two of these three Lake Thun sediment cores at around 1950, but were first observed in the other core as early as the late-1800s, presumably as a result of contamination arising during the extrusion and laboratory analysis of the third core (Bogdal et al., 2008). In three sediment cores from Lake Michigan and one from Lake Huron, PCB fluxes increased rapidly following emergence in the 1930s until peaking in the late 1970s, followed by an initial decline before fluxes again increased to levels close to historical maximum fluxes in surficial sediment. In contrast, PCB input fluxes kept increasing in two other cores from Lake Huron until the 1990s, before declining noticeably through to surficial sediments (Song et al., 2005b). In Lake Superior, PCB inputs were first observed in 1880-1920 (again presumably attributable to sampling and analytical artefacts) with peak fluxes observed in the mid-1980s (n=4) followed by clear decreases thereafter (Song et al., 2004). With respect to trends in other matrices, Law et al. (2012) reported that the decline in PCB concentrations in porpoises from UK coastal waters to about 1998 has now plateaued over the period 1992-2008.

4.3.1.2 PBDEs

For the tri- through hexa-BDE congeners that comprise the Penta-BDE formulation, BDE-183 as the principal component of the Octa-BDE formulation, and BDE-209 as presumed marker of Deca-BDE commercial formulas; the first signs of their appearance in our English freshwater lakes were clearly observed from the mid-1960s to around 1970. Fluxes of tri-hexa-BDEs (essentially equating to Penta-BDEs) peaked in the late 1990s at five out of seven English lakes in this study, though followed by a modest subsequent increase in contamination in surface sediment at some sites. These observations appear encouraging signs that contamination has peaked and is now falling. This is likely a reflection of recent control measures on new production and usage of Penta-BDE in Europe since EU restrictions were introduced in 2004.

Broadly consistent with our observations, Zegers et al. (2003) reported the emergence of Penta-BDE related congeners in lakes from Western Europe at the beginning of the 1970s, with concentrations in top layers representing 1995 and 1997 levelling off in sediment cores from the western Wadden Sea (Netherlands) and Lake Woserin (freshwater, Germany), but still increasing in the sediment core from Drammenfjord in 1999. Similarly, concentrations of Σtri-hepta-BDEs

increased consistently after first emergence, but levelled off from the mid-1990s up to 2001 in Greifensee, a small urban lake in Switzerland (Kohler et al., 2008). In slight contrast, concentrations of Σtri-hepta-BDEs showed generally increasing trends in two out of three sediment cores from Lake Thun, Switzerland following their initial emergence in the late 1980s or early 1990s (Bogdal et al., 2008). In North America, the first occurrences of Σtri-octa-BDEs in cores from Lake Michigan (n=3) and Lake Huron (n=3) varied but occurred mainly in the 1940s and 1950s, and have generally increased rapidly to a peak in surficial sediments, with the slight exception of one core in which a decline was observed in the top layer (Song et al., 2005b). With respect to trends in other matrices, Law et al. (2010) reported Σtri-hexa-BDEs concentrations in porpoises from UK coastal waters to increase to around 1998 over the period 1992-2008. However, no sign of decreasing concentrations of banned BDE congeners was observed in a study of PBDEs in snow melt from the Devon Ice Cap in Nunavut (Canada) over the period 1993/4-2007/8 (Meyer et al., 2012), reflecting the potential delayed response of some environmental compartments to recent control measures, coupled with continuing emissions from the remaining reservoir of PBDEs both in use and entering the waste stream.

While BDE-183 showed a mixed picture with respect to temporal trends across all sites in this study, BDE-209 displayed generally smooth increases since its initial emergence at most sites around 1960, and showed no obvious levelling off trend except at CRAZ, the most remote site in the current study. This is consistent with the earlier introduction of use restrictions on Octa-BDE compared to Deca-BDE. For comparison, in some contrast with our findings, BDE-209 concentrations were reported to be decreasing in the top layers (representing 1995/7/9) of three sediment cores from the western Wadden Sea (Netherlands), Lake Woserin (freshwater, Germany), and Drammenfjord (Norway) (Zegers et al., 2003). In Lake Michigan (n=3) and Lake Huron (n=3), input fluxes of BDE-209 increased rapidly following emergence in the 1960s-1970s in most sediment cores, and peaked in surficial sediments in four of six cores (Song et al., 2005b). Similar observations were made for PBDE trends in Lake Superior in an earlier study (Song et al., 2004). Moreover, BDE-209 concentrations in North American outdoor air reached a steady state at most study sites between 2005 and 2011 (Ma et al., 2013). However, this more rapid response of the atmosphere is likely attributable to the more rapid mixing time of this compartment. In two out of three sediment cores from the Pearl River estuary in China, BDE-209 showed only a minor increase following first emergence in the mid- to late-1970s, followed by a rapid increase from

around 1990, and a decline observed in surface layer sediment (Chen et al., 2007). In the UK, BDE-209 and Σ_{16}penta-nona-BDEs trends varied in the six sediment cores collected in 2002/3 from the inner Clyde Estuary (Vane et al., 2010). To be specific, four cores showed generally increasing trends following their first emergence, with various trends observed in the top layer. Likely a reflection of the highly industrialised nature of the Clyde river, historical concentrations of Σ_{16}BDEs (BDE-209 excluded), BDE-209, and Σ_{16}BDEs (BDE-209 included) in the above six sediment cores ranged from 1 to 307, 1 to 2337, and 1 to 2645 ng g^{-1} dw, respectively (Vane et al., 2010), with the upper range concentrations significantly higher than those observed in any of the seven English freshwater lakes in this study. Moreover, four sediment cores from the Garroch Head sewage disposal site in the Firth of Clyde showed extremely high concentrations of BDE-209 (2.3 to 98125 ng g^{-1} dw) but comparable Σ_{17}BDEs (BDE-209 excluded) levels (Webster et al., 2008) to our study. Finally, concentrations of Deca-BDE increased rapidly following first emergence in the mid-1960s in Lake Greifensee and reached 7.4 ng g^{-1} dw in 2001 (Kohler et al., 2008). In conclusion, temporal trends in BDE-209 contamination in English freshwater lakes seem broadly consistent with previous studies elsewhere in the world.

4.3.1.3 HBCDs

At most of the locations studied in this chapter, HBCD concentrations have increased rapidly post-emergence in the 1960s before peaking in the late 1980s-early 1990s. While at the most contaminated site (EDGB, Birmingham), HBCD contamination increased throughout the monitored period and showed no sign of decreasing or levelling off; HBCD contamination at most sites has declined considerably after the point of peak inputs. Consistent with our observations of temporal trends in English lakes, HBCD levels increased rapidly to 2.5 ng g^{-1} dw in 2001 in a sediment core from Lake Greifensee in Switzerland (Kohler et al., 2008). Farther afield, HBCDs in three sediment cores from Tokyo Bay increased steadily following their emergence in sediment slices from the late 1960s and early 1970s, and continued to increase through to the surficial sediments, in which concentrations were 0.73 to 2.1 ng g^{-1} dw (Minh et al., 2007). In one of the three sediment cores from Lake Thun, Switzerland, HBCD contamination was stable from the mid-1970s up to around 1990, but increased rapidly thereafter up to 2005 (Bogdal et al., 2008). In contrast, another of these cores displayed a rapid increase in HBCD concentrations between the mid-1980s and the late 1990s, followed by a steady decrease

thereafter (Bogdal et al., 2008). Temporal trends were also investigated in archived biological samples, e.g., a significant decrease of HBCDs after a distinct peak at around 2000 in herring gull eggs on three German islands was reported (1988-2008; Esslinger et al., 2011). Moreover, Law et al. (2012) reported a sharp increase in HBCDs in blubber of harbour porpoise in the UK between 2000 and 2001, followed by a significant fall between 2003 and 2004, which the authors attributed to the closure in 2003 of an HBCD production facility in northeast England coupled with reduced HBCD sales in the UK leading up to that point.

4.3.1.4 NBFRs

Twelve NBFRs were found above detection limits in sediment from at least one lake up to all 7 lakes in this study depending on the specific compound. The 12 NBFRs are: TBPH, PBEB, TBB, TBBPA-DBPE, BTBPE (also known as TBE), DBDPE, HCDBCO, TBECH, HBB, PBCC, PBBB, and (a- and s-)DP. Of these, TBPH, TBBPA-DBPE, PBEB, HCDBCO, TBB, BTBPE, and DBDPE were selected for detailed discussion here given their relatively elevated contribution to total NBFR concentrations and more frequent detection at our sites. With the exception of TBPH, all NBFRs detected in the current study showed consistently lower concentrations than BDE-209 in the same cores. This is broadly consistent with the study of Yang et al. (2012), who reported that BDE-209 concentrations in sediments from the Great Lakes were at least one order of magnitude higher than those of the 13 NBFRs analysed in the same samples. However, no information on TBPH was available as it was not targeted in their study. In the current study, concentrations of TBB (except at the EDGB site), BTBPE, and DBDPE were similar to those of BDE-183, reflecting potentially a similar extent and level of production and usage. While in inland and coastal surficial sediments from southern Africa, BDE-209 concentrations generally exceeded TBPH, BTBPE, DBDPE, and TBB, with concentrations (average) ranging from below quantification limits to 44500 (3208), 899 (96), 616 (34), 1840 (171), and 13900 (545) ng g^{-1} TOC, respectively (La Guardia et al., 2013).

TBPH As shown in Figure 4.1, TBPH is clearly the dominant NBFR in our English freshwater lakes, displaying consistently increasing concentrations since its emergence (which occurred at most sites around the mid-1970s) through to the present. Consistent with our observations at all studied English freshwater lakes, Ma et al. (2013) reported an increasing trend in atmospheric concentrations of TBPH over the period 2005-2011 (inclusive) at three of five monitored sites in

the Great Lakes region. However, previous studies on NBFRs in sediments have rarely targeted TBPH, which prevents further comparison with trends elsewhere. And to the best of our knowledge, it appears that our study is the first report of temporal trend of TBPH in sediments worldwide.

PBEB PBEB was used as an additive flame retardant in thermoset polyester resins (circuit boards, textiles, adhesives, wire and cable coatings, and polyurethanes) and thermoplastic resins during the 1970s and 1980s. Production in North America ranged between 45 and 450 tons in 1977, but its manufacture was discontinued at the end of the 1980s (USEPA, 1985 and 1988). In general, PBEB emerged at most of our sites around the mid-1960s, peaked at most sites between the mid-1980s to late 1990s, and decreased steadily thereafter. However, concentrations are still increasing at EDGB. In North America, a similar contrast between decreasing trends in atmospheric PBEB concentrations at most sites in the most recent few years, and a still increasing concentration trend at the site with highest concentrations was also reported by Ma et al. (2013). These observations of contrasting spatial trends are not inconsistent with the report that PBEB was below detection limits in a sediment core taken in 2004 from Lake Michigan, but detected in both the gas and particulate phases of ambient air from Chicago while PBEB levels in the remaining air samples were low but detectable (Hoh et al., 2005).

BTBPE BTBPE is an additive BFR first marketed in the mid-1970s which by the mid-2000s found some limited use (Hoh and Hites, 2005) as a replacement for the Octa-BDE formulation. In our study, BTBPE emerged at most sites in the late 1970s or early 1980s; thenceforth concentrations remained generally stable or increased only moderately at five out of seven sites. The exceptions are EDGB and PFLE which are amongst the most contaminated sites and where concentrations have increased significantly since the mid-1980s through to the present. Consistent with our observations at sites other than EDGB and PFLE, Hoh et al. (2005) reported that in a Lake Michigan sediment core taken in 2004, BTBPE first emerged in 1973, then increased through to 1985 before stabilising through to the early 1990s - the last data point of the study. Similarly, BTBPE concentrations in North American air (both vapour and particle phases) and precipitation showed decreasing or stable trends between 2005 and 2011 (Ma et al., 2013). In contrast - but consistent with observations at our EDGB and PFLE sites - BTBPE concentrations in Lake Ontario sediment cores taken in 2004, increased continuously to the present from their

emergence around the mid-1980s (Qiu et al., 2007). Similarly, a study of Great Lakes sediment cores revealed concentrations of BTBPE at all locations studied (with the exception of Lake Erie) to increase generally following its first detection in the 1970s (Yang et al., 2012).

DBDPE DBDPE is an additive BFR applied as an alternative to the technical Deca-BDE formulation due to their very similar chemical structures (Kierkegaard et al., 2004). Compared with BDE-209, DBDPE emerged 15-35 years later in this study, but has continued to increase at all sites since first emergence. For comparison, Yang et al. (2012) reported DBDPE to emerge 10-20 years after BDE-209 in sediment cores from the Great Lakes.

Other NBFRs Concentrations of TBB generally increased at most sites at various rates with some fluctuations since its first emergence during the early 1960s and mid-1980s, while remained stable at SLT and WAKE after a few years of its first emergence. TBBPA-DBPE is an additive BFR, concentrations of which generally increased at most of our monitored English lakes since its first emergence in 1970s. From early 1980s onward, TBBPA-DBPE concentrations remained stable at CRAZ and HOLT up to late 1990s, and remained stable through to the present at EDGB and SLT. Concentrations of TBECH were lower than the "legacy" and seven selected NBFRs discussed in this chapter. Consistent with this, Yang et al. (2012) also reported lower concentrations of TBECH than of BTBPE, DBDPE, and HBCD in sediments from the north Great Lakes, reflecting the former's lower production volume. HCDBCO concentrations have peaked in the late 1960s-early 1980s and have declined after the point of peak inputs at most of the locations studied in this chapter. While at the most contaminated site (EDGB), HCDBCO contamination increased throughout the monitored period and showed sign of levelling off in top layer. Regarding DPs, while there is evidence of extensive use in North America (Sverko et al., 2008); DPs were only detected at four out of seven sites in this study, with maximum concentrations of 0.53 ng g^{-1} dw (1.60 ng g^{-1} TOC) observed at EDGB, more than 200 times lower than BDE-209 at the same site. While ΣDP in Niagara River suspended sediments revealed a clear decreasing trend over the period of 1980-2002 (falling from 89 to 7 ng g^{-1} dw over this period) (Sverko et al., 2008); no clear temporal trends were observed for English freshwater lakes.

In summary, while some NBFRs were found at considerable concentrations in this study, indicating their ubiquitous and widespread use, other NBFRs were not detected or were present at

low levels only. This may be attributed to one or more of the following factors: 1) their limited production, market demand and use in the UK; 2) their limited tendency for release from industrial and commercial products and subsequent migration into indoor and outdoor environments; 3) a relatively weak partitioning tendency into sediments, e.g., among the non-detected NBFRs in this study, TBP and ATE are known to have much higher vapour pressure (0.41 and 0.05 Pa at 25℃, respectively) and relatively lower log K_{OW} values (4.33 and 4.97, respectively; Covaci et al., 2011); and 4) unknown matrix interferences under the analytical conditions used.

4.3.2 Temporal Trends in the Relative Abundance in English Lake Sediment of Exemplar "Classic" POPs, "Legacy" BFRs, and NBFRs

The previous sections reveal that ΣPCBs, BDE-209, and TBPH were the principal POPs detected in the sediment cores taken in this study, and represent "classic" POPs, "legacy" BFRs, and NBFRs, respectively. Σtri-hexa-BDEs are also important "legacy" compounds, though with historically consistently lower concentrations in English lake sediments than the other three principal compounds highlighted. Figure 4.2 compares the trends for each of these three contaminant groups at three relatively highly contaminated and three less contaminated sites. Regarding the three principal compounds, an interesting observation was that concentrations of BDE-209 exceeded PCBs during the mid-1980s-around 2000 at the three most contaminated sites (EDGB, MARM and PFLE, listed in the right column). At the other less contaminated sites: concentrations of BDE-209 in the very recent core slices just slightly exceed those of ΣPCBs at SLT, and have been consistently lower than those of ΣPCBs at CRAZ and WAKE over the period 1950-2011/2. However, given the apparent downward trend of PCBs and upward trend of BDE-209, it is thought very likely that BDE-209 will exceed ΣPCBs at WAKE in the coming years, though this is not clear at CRAZ. The more rapid emergence at more urbanised lakes of BDE-209 at higher concentrations than ΣPCBs, than seen at less urbanised locations; is consistent with the hypothesis that BDE-209 has a lower capacity than PCBs for long-range environmental transport from source regions.

Of particular note, TBPH concentrations first exceeded those of PCBs at all sites in this study at various points ranging from the late 1970s to the late 2000s (mainly in the 1990s). As with BDE-209, concentrations of TBPH exceeded those of PCBs at generally an earlier date at more

urbanised sites (late-1970s-late 1990s) than at relatively less contaminated sites (early 1990s-late-2000s). Moreover, TBPH concentrations exceeded those of BDE-209 almost since its emergence during the late 1960s-mid-1980 at relatively less contaminated sites, and at around mid-1970 to mid-1990s at more urbanised sites. These exciting observations reveal extensive use of TBPH in the UK.

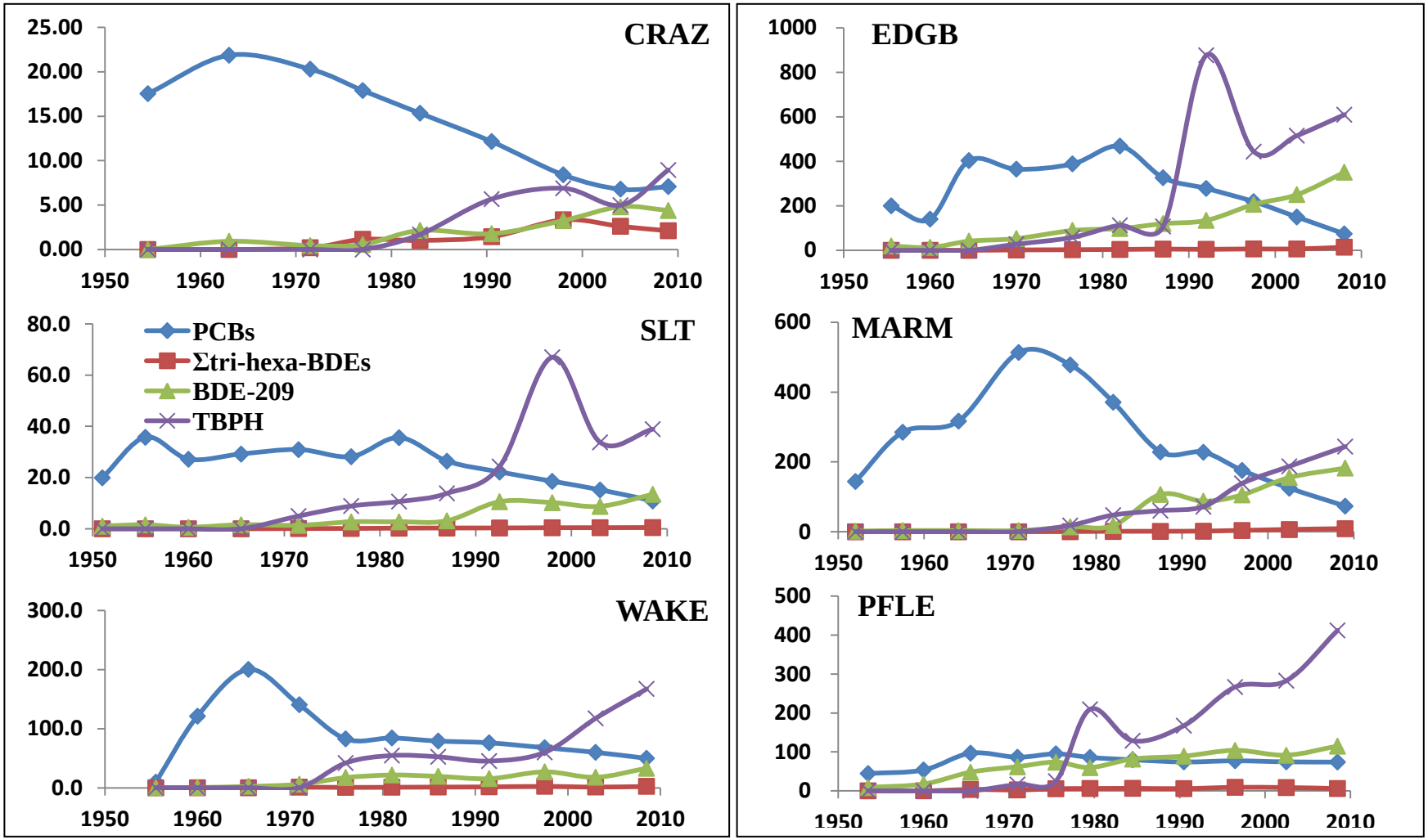


Figure 4.2 Highlighted comparisons of temporal trends in PCBs, Σtri-hexa-BDEs, BDE-209, and TBPH in English freshwater lakes, 1950-2011/2, with relatively less urbanised lakes shown on the left, and highly urbanised lakes on the right

4.4 Input Fluxes, Inventories, and Possible Influencing Factors

4.4.1 Temporal and Spatial Trends in Input Fluxes

While temporal trends in POPs concentrations expressed on an organic carbon-normalised basis display well the historical changes in their contamination levels over a known period (at five year intervals in this study); calculation of input fluxes gives additional information on historical changes in intensity of inputs into the monitored lakes. Thus, temporal trends in POPs input fluxes (ng cm^{-2} y^{-1}) were also investigated. Input fluxes were calculated using equation 4.1 below:

Input flux=[(Concentration (dry mass basis)*Dry Mass)/Sedimentation Years]/Surface Area (4.1)

Historical inputs of target POPs showed generally similar temporal trends to those indicated for concentrations, as a consequence of the generally limited intra-site temporal changes in sedimentation rates. Overall, POPs input fluxes displayed spatial patterns similar to those based on TOC-normalised concentrations, with highest input fluxes generally found at EDGB and MARM, and lowest at CRAZ and SLT. However, some differences were observed due to inter-site variations in sedimentation rates. Sedimentation rates in this study were: MARM>WAKE>HOLT>PFLE≈EDGB≈SLT≈CRAZ (see Table 4.1). Thus, compared with POPs concentrations, input fluxes were relatively elevated at the MARM, WAKE and HOLT sites. The elevated annual inputs of sediment mass at MARM (around 3 to 7 times of those observed at other sites) are a contributory factor in the elevated input fluxes (ng cm^{-2} y^{-1}) of POPs at this site compared to others.

4.4.2 Profiles and Spatial Trends in Inventories, and Potential Influencing Factors

4.4.2.1 Profiles in POPs Inventories

POPs inventories were investigated to gain more information on the mass of POPs present in the lakes in this study. POPs inventories were calculated using equation (4.2):

Inventory=Σ[Concentration (on dry mass basis)*Dry Mass Density*Segment Thickness] (4.2)

The detection rate of PCBs across all sites was 100%; this, combined with their marked presence in the earliest sediment slices leads to the assumption that minor concentrations of PCBs would

likely be detected in sediment cores from English freshwater lakes in slices dated before 1950. The appearance of PCBs prior to the monitoring period in this study thus leads to a slight underestimation of PCB inventories in English lakes. Despite this, Figure 4.3 shows PCBs are the dominant contaminant monitored at CRAZ, HOLT, MARM, SLT, and WAKE; while TBPH dominated at EDGB and PFLE. TBPH was generally the second most prevalent contaminant with inventories exceeding those of BDE-209 in all studied English lakes by a factor of 1.1 to 6.1 times (average$\pm\sigma_{n-1}$ 2.9±1.7). It is unsurprising that PCBs are the main compound in terms of inventory given their earlier production and longer history of use. However, it is surprising that TBPH is not far behind despite the perceived more recent onset of its production and use. Note that the elevated annual inputs of sediment mass at MARM, as for input fluxes (ng cm^{-2} y^{-1}) of POPs at this site compared to others, are also a contributory factor for the elevated inventories at MARM.

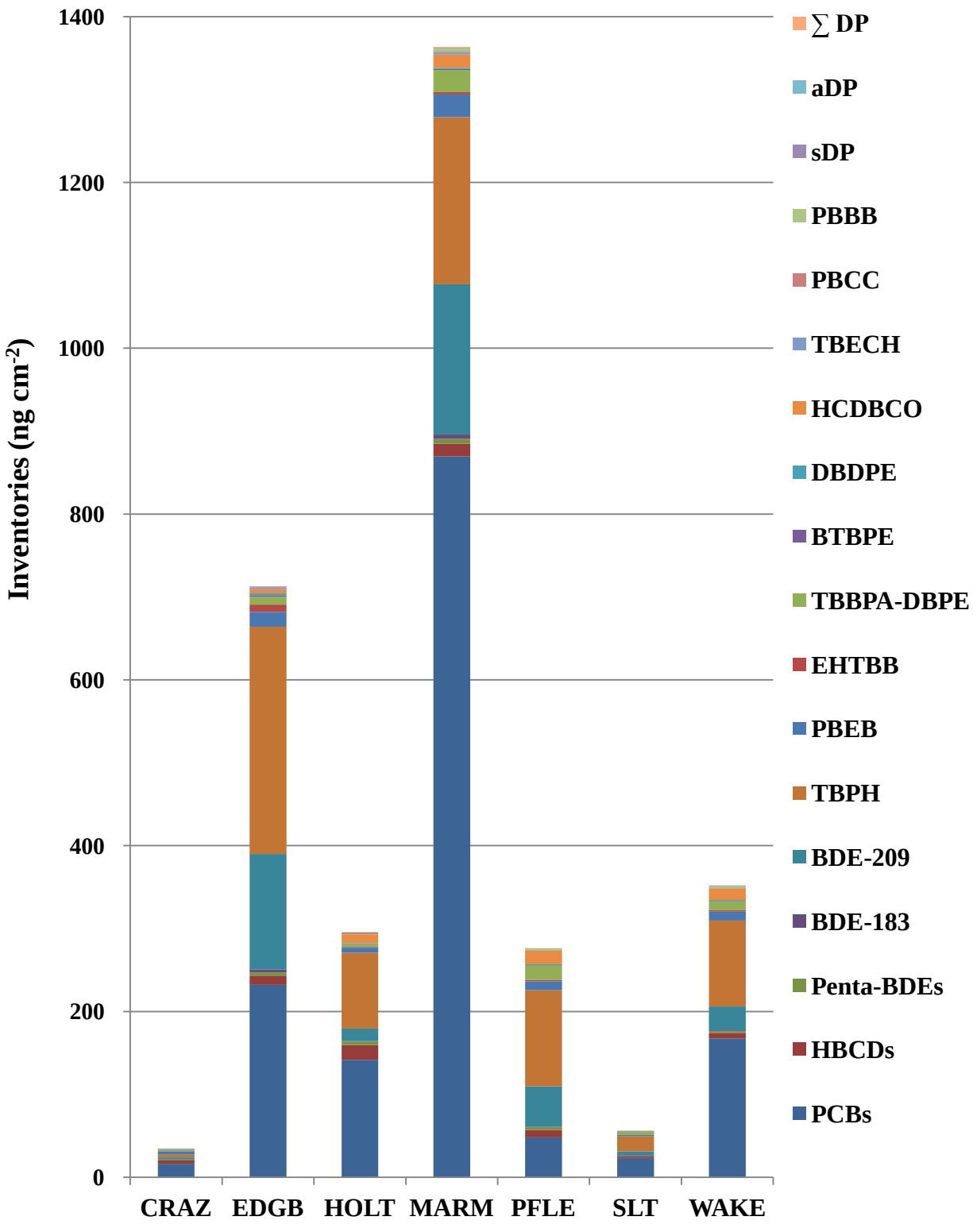


Figure 4.3 Inventories (ng cm^{-2}) of target compounds in English freshwater lakes, ~1950-2011/2

4.4.2.2 Estimated POPs Burden in the UK

To provide an - albeit relatively crude - estimate of the burden of our target POPs in the UK environment, the average POPs inventories (~1950-2011/2) obtained from our seven monitored English lakes and a UK surface area of 2.4361 x 10^{11} m^2 were used (see Table 4.3). As highlighted earlier, due to the potential minor occurrence of PCBs in lake sediments prior to ~1950s, the PCB burden in the UK is likely slightly underestimated. The estimated PCB burden in the British environment is 521 tons. Consistent with these estimates, Harrad et al. (1994) estimated the PCB burden in the UK soil (top 5 cm) to be 370 tons, based on the data of Alcock et al. (1993) from a survey of a mix of rural and urban soils (n=39) from northwest England. Due to the likely presence of PCBs at soil depths below 5 cm, the actual burden was likely at least twice the estimated value (Harrad et al., 1994). In conclusion, of the estimated 40,000 tons PCBs sold in the UK since 1954 (Harrad et al., 1994), around 1% has escaped and still remains in the outdoor UK environment. This illustrates how historical production and usage of PCBs still influences the environment today. It should also be noted that there likely remains a substantial but as yet unquantified reservoir associated with PCB-treated materials in the built environment.

TBPH was the second most abundant POP quantified in the UK environment following not far behind PCBs, with an estimated burden of 281 tons. BDE-209 was the third most abundant POP in this study with an estimated burden of 147 tons, approximately half that of TBPH. Our estimated UK burdens of the remaining target compounds were significantly lower than those of PCBs, BDE-209, and TBPH, with their predominance as follows: (HBCDs, PBEB, TBBPA-DBDPE, and HCDBCO) > (Σtri-hexa-BDEs, and TBB) > (BDE-183, BTBPE, DBDPE, TBECH, PBCC, and PBBB) > (HBB, and ΣDPs). As illustrated with POPs concentrations, with the exception of TBPH, all NBFRs detected in the current study showed lower burdens in the UK environment than PCBs and PBDEs, indicating their relatively lower production and use in the UK.

Table 4.3 Average POPs inventories in English freshwater lakes (n=7) and estimated UK surface burdens

Compounds	Average Inventories (ng cm^2)	UK Surface Burden (t)	%Total UK POPs Burden
ΣPCBs	214	521	48.5
ΣHBCDs	9.38	22.9	2.12
Σtri-hexa-BDEs	3.21	7.82	0.73
BDE-183	1.53	3.73	0.35
BDE-209	60.1	147	13.6
TBPH	115	281	26.1
PBEB	11.1	27.0	2.51
TBB	2.50	6.09	0.57
TBBPA-DBPE	10.3	25.0	2.32
BTBPE	0.73	1.78	0.17
DBDPE	1.03	2.50	0.23
HCDBCO	8.86	21.6	2.01
TBECH	0.83	2.01	0.19
HBB	0.04	0.10	0.01
PBCC	0.71	1.73	0.16
PBBB	1.38	3.37	0.31
sDP	0.23	0.56	0.05
aDP	0.03	0.07	0.01
ΣDP	0.26	0.63	0.06

4.4.3 Inter-Site Variability of POPs Inventories

In this study, the ratios of highest to lowest inventories between sites were 7, 28, and 54 for HBCD, Σtri-hexa-BDEs, and ΣPCBs, respectively. These were substantially lower than the values observed for BDE-209 (82) and TBPH (79), demonstrating greater spatial variability for these two contaminants. This is consistent with the hypothesis that BDE-209 and TBPH have limited capacity for long-range atmospheric transport.

Inventories of BDE-209 in this study were around one order of magnitude higher than that of Σtri-hexa-BDEs and BDE-183 combined; an observation consistent with that made previously in Lake Superior (Song at al., 2004). Also broadly consistent with the observations of Song et al. (2004) for Lake Superior, was the relatively constant contribution of BDE-209 to ΣPBDE inventories across all sites in this study. Despite covering seven different lakes, the percentage contribution of BDE-209 to ΣBDEs ranged from 60 to 96% compared with the range for several different locations in Lake Superior of 83-94% (Song et al., 2004).

4.5 POPs in Surficial Sediments

While inventories provide insights into the historical accumulation of POPs in English lakes, surficial concentrations inform about contemporary contamination. Concentrations of monitored POPs in surficial sediment (defined as that in the most recent sediment layer representing approximately the last 5 years) are summarised in Table 4.4, with the spatial distribution of major surficial POPs contaminations illustrated in Figure 4.4.

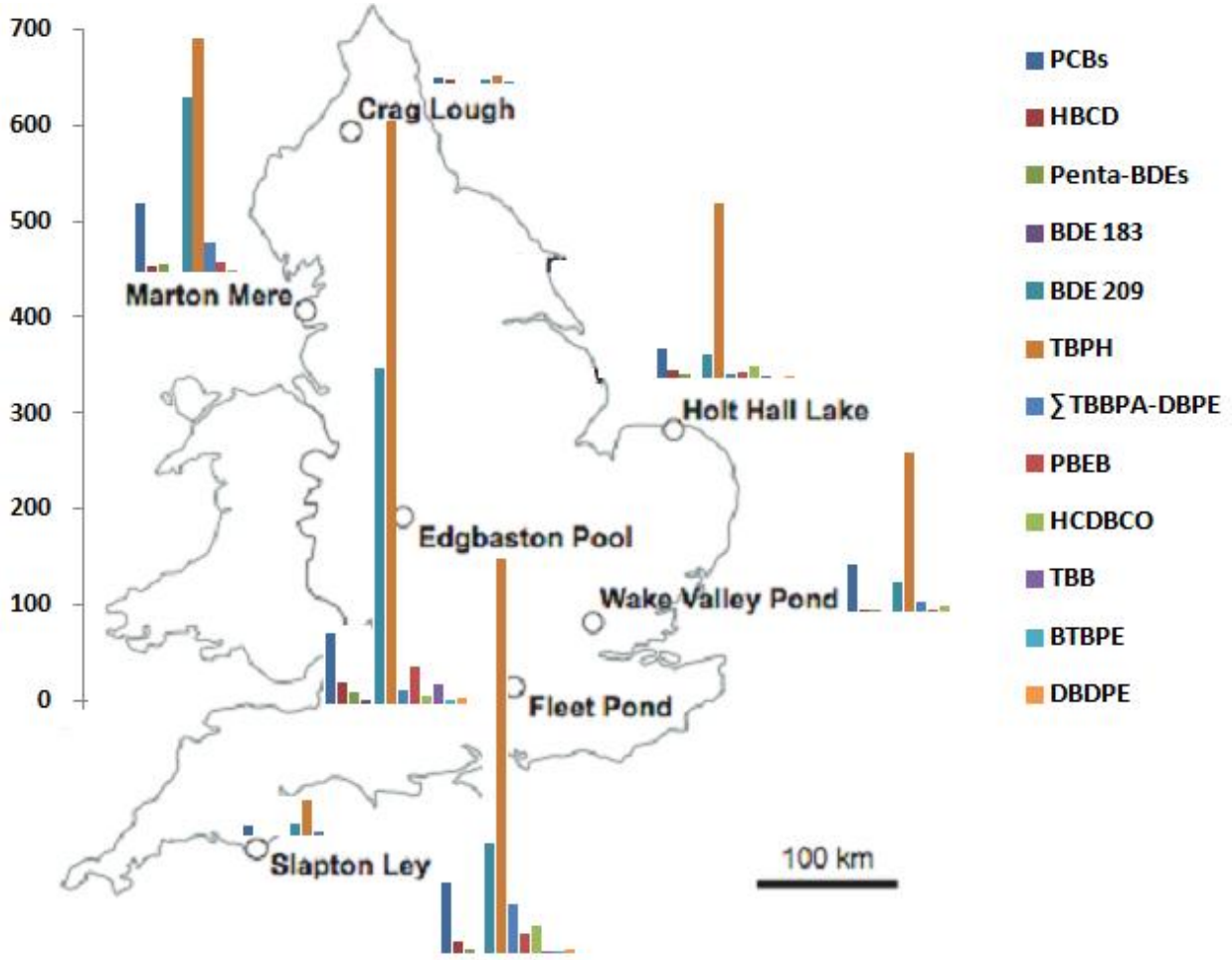


Figure 4.4 Concentrations (ng g^{-1} TOC) and distributions of target legacy compounds and selected NBFRs in surficial sediment layers from seven English freshwater lakes

Table 4.4 Concentrations[a] of POPs in surficial sediments expressed on both dry mass (ng g^{-1} dw) and TOC normalised basis (ng g^{-1} TOC, in parentheses)

Compounds	Sampling Sites (Year Range)						
	CRAZ (2007-11)	**EDGB** (2005-11)	**HOLT** (2006-11)	**MARM** (2006-12)	**PFLE** (2006-11)	**SLT** (2006-11)	**WAKE** (2006-11)
ΣPCBs	2.64 (7.08)	24.4 (74.0)	10.1 (32.4)	10.9 (73.5)	13.5 (74.0)	3.69 (10.8)	13.6 (49.9)
ΣHBCDs	1.61 (4.33)	7.87 (23.9)	3.01 (9.66)	1.00 (6.76)	2.45 (13.4)	0.42 (1.22)	1.13 (4.17)
Σtri-hexa-BDEs	0.79 (2.11)	4.65 (14.1)	1.82 (5.86)	1.32 (8.89)	1.10 (6.00)	0.16 (0.47)	0.66 (2.43)
BDE-183	0.09 (0.24)	1.79 (5.45)	0.18 (0.59)	0.28 (1.91)	0.19 (1.02)	<0.12	0.17 (0.63)
BDE-209	1.63 (4.39)	116 (351)	8.30 (26.7)	27.1 (183)	21.0 (115)	4.57 (13.5)	8.93 (32.9)
TBPH	3.33 (8.95)	201 (609)	57.0 (183)	36.2 (244)	75.3 (412)	13.2 (38.9)	45.5 (167)
PBEB	0.76 (2.05)	13.1 (39.8)	2.37 (7.63)	1.66 (11.2)	3.97 (21.8)	0.42 (1.23)	1.05 (3.88)
TBB	0.21 (0.56)	7.37 (22.4)	0.75 (2.42)	0.30 (2.00)	0.58 (3.17)	0.31 (0.90)	0.41 (1.51)
TBBPA-DBPE	1.48 (3.98)	5.15 (15.7)	1.54 (4.96)	4.70 (31.7)	9.46 (51.8)	1.93 (5.66)	3.08 (11.3)
BTBPE	0.29 (0.79)	1.77 (5.38)	0.23 (0.74)	0.14 (0.94)	0.54 (2.96)	0.04 (0.12)	0.29 (1.08)
DBDPE	0.47 (1.27)	2.09 (6.35)	0.76 (2.44)	0.32 (2.19)	0.87 (4.79)	0.28 (0.82)	0.55 (2.01)
HCDBCO	0.15 (0.39)	2.97 (9.03)	3.96 (12.7)	0.53 (3.57)	5.44 (29.8)	0.12 (0.34)	2.11 (7.77)
TBECH	0.12 (0.33)	0.96 (2.91)	0.15 (0.49)	0.35 (2.33)	0.13 (0.69)	0.07 (0.20)	0.12 (0.43)
HBB	<0.01	0.24 (0.72)	<0.01	<0.01	<0.01	<0.01	<0.01
PBCC	0.79 (2.12)	1.45 (4.39)	1.26 (4.04)	0.13 (0.85)	0.06 (0.35)	<0.01	<0.01
PBBB	0.26 (0.69)	0.11 (0.32)	0.59(1.88)	0.94 (6.37)	0.61 (3.33)	0.11(0.32)	0.51 (1.89)
sDP	<0.01	0.40 (1.21)	<0.01	0.06 (0.41)	0.14 (0.77)	<0.01	0.11 (0.41)

Compounds	CRAZ	EDGB	HOLT	MARM	PFLE	SLT	WAKE
aDP	<0.01	0.13 (0.39)	<0.01	<0.01	<0.01	<0.01	<0.01
ΣDP	<0.01	0.53 (1.60)	<0.01	0.06 (0.41)	0.14 (0.77)	<0.01	0.11 (0.41)

[a] Limit of Quantification (LOQ, ng g^{-1} TOC) was reported where compound was found below detection limits

4.5.1 Discussion on POPs in Surficial Sediments

Unless otherwise stated, the concentrations of POPs referred to in the following discussion are those normalised to TOC content rather than dry mass. Regarding spatial trends, the highest concentrations of classic POPs/legacy BFRs in surficial sediments were consistently found at EDGB, whereas MARM and PFLE also showed PCB concentrations as high as at EDGB. In contrast, the lowest concentrations were observed at either CRAZ or SLT, both of which are rural/remote sites. For NBFRs, the highest concentrations of TBPH, PBEB, TBB, DBDPE, BTBPE, and TBECH in surficial sediment layers were all found at EDGB.

Figure 4.5 shows the relative contributions of major POPs found in surficial sediments from our English lakes. Across all sites, their predominance was generally as follows: TBPH>BDE-209>PCBs>TBBPA-DBPE>PBEB≈ΣHBCDs>HCDBCO≈Σtri-hex-BDEs>TBB≈DBDPE> BTBPE≈BDE-183. It is striking that TBPH was the dominant contaminant monitored in all surficial sediment layers analysed; displaying concentrations that were between 1 and 7, and 1 and 8 times those of BDE-209 and PCBs at the seven sites, respectively; while PBEB, TBB, TBBPA-DBPE, HCDBCO and DBDPE showed generally comparable concentrations to those of HBCDs and Σtri-hexa-BDEs. In contrast, BDE-209 is one or two orders of magnitude more abundant than either Σtri-hexa-BDEs or BDE-183. Concentrations of BDE-209 (351 ng g^{-1} TOC) in surficial sediment almost reach the highest historical PCB concentration (468 ng g^{-1} TOC) at EDGB, and are 1.2 times the peak concentration of PCBs at PFLE. Strikingly consistent with these observations, in the early 2000s, concentrations of BDE-209 in Lake Superior had also reached or even exceeded the historical peak PCB concentrations recorded (Song et al., 2004).

Combined, while our data shows the continuing long-term legacy of past PCB use, it suggests a relatively rapid response to: recent curbs on the use of some BFRs (e.g. the Penta-BDE formulation), the continuing extensive use of Deca-BDE, and the rising use of some NBFRs; in particular TBPH. With respect to NBFRs, TBPH was the most abundant compound, while the relative abundance of our other target NBFRs varying at each site. Studies on NBFRs in sediment are extremely rare. The only related study of which we are aware is that, in inland and coastal surficial sediments from southern Africa, BDE-209 concentrations generally exceeded those of TBPH, BTBPE, DBDPE, and TBB; with concentrations (average values in parentheses) for these 5 contaminants respectively ranging from below quantification limits in each case to 44500

(3208), 899 (96), 616 (34), 1840 (171), and 13900 (545) ng g^{-1} TOC. In the same study, the average concentration of ΣHBCDs was about half that of BDE-209 (La Guardia et al., 2013). This compares with our study in which BDE-209 concentrations in different core slices exceeded those of HBCDs by factors of between 1 and 27 (mean=10). The different contaminant pattern of POPs between inland and coastal sediments from southern Africa and English lakes in this study likely implies international variations in the production and use of these compounds. Several studies of indoor dust were also selected for comparison to this study. These studies reported the mean relative abundance of their targeted NBFRs was: TBB> TBPH> DBDPE> BTBPE (home vacuum bag and main living area), and DBDPE> TBPH> TBB> BTBPE (bedroom) in US house dust (Stapleton et al., 2008), and DBDPE> BTBPE> TBBPA-DBPE> TBPH> TBB in dust from an e-waste recycling facility in Thailand (Ali et al., 2011b).

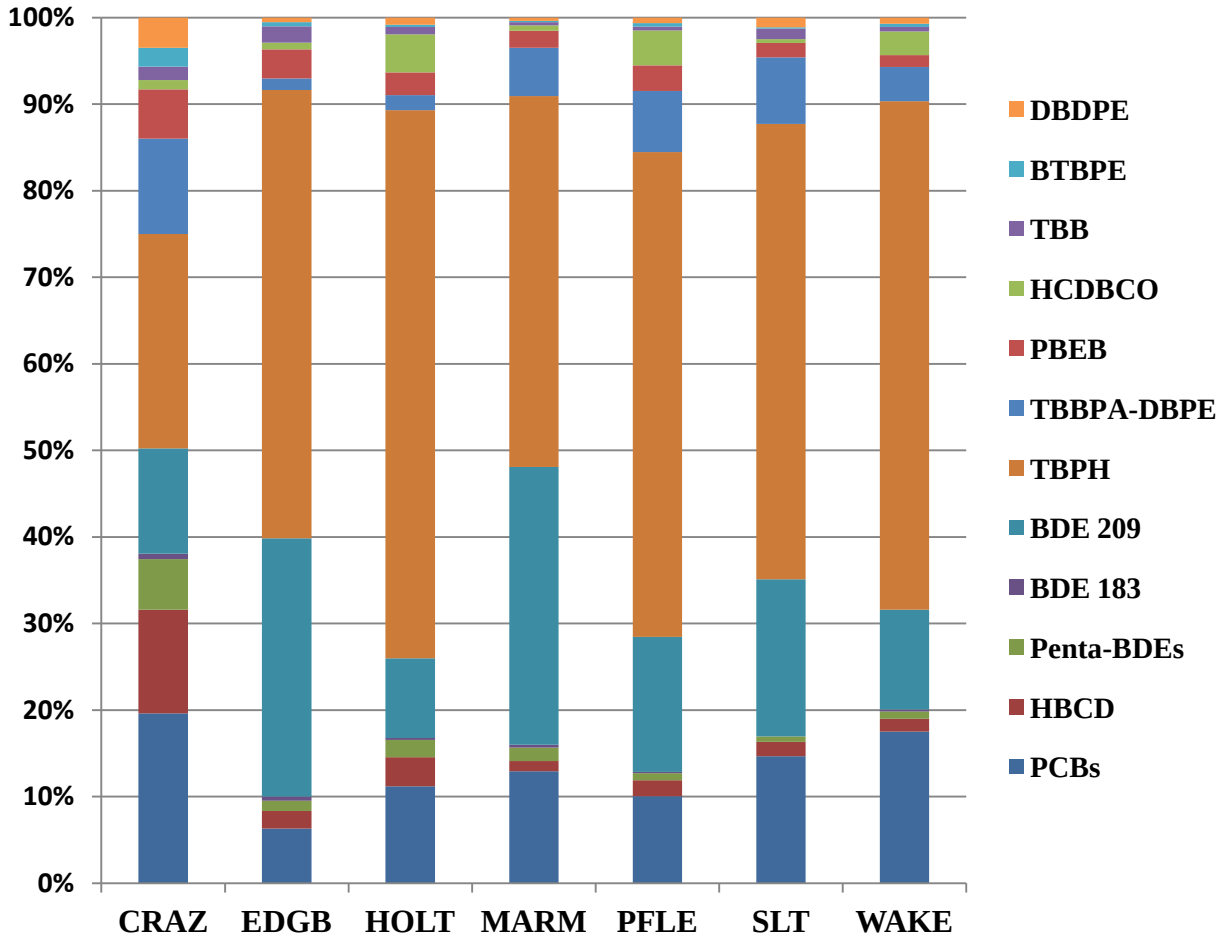


Figure 4.5 Relative abundances of major POPs found in surficial sediments from seven English freshwater lakes, 2005/6/7-11/2

Table 4.5 Summary of concentrations (ng g^{-1} dw) of ΣPCBs, ΣHBCDs, and ΣPBDEs in surficial sediments (mean values in parentheses)

Description (Sampling Year/Year Range)		ΣPCBs	ΣHBCDs	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
Seven English Freshwater Lakes	***Top layer (2006-2011)***	***2.64-24.4 (11.2)***	***0.42-7.87 (2.50)***	***0.16-6.44 (1.89)***	***1.63-116 (26.7)***	***Current Study***
	Second layer (2001-2005)	***2.30-47.3 (17.1)***	***0.79-9.76 (4.29)***	***0.14-2.85(1.36)***	***1.62-79.1 (18.8)***	
	Third layer (1995-2000)	***3.45-63.8 (22.4)***	***0.74-8.15 (2.71)***	***0.13-3.13 (1.42)***	***1.33-60.4 (15.5)***	
European sediments						
Tees Estuary, a highly polluted area downstream of a BFR manufacturing plant in the UK				Up to 368 for BDE-47, and 898 for BDE-99		Allchin et al., 1999
Cork Harbour, Ireland (2002)		0.02-0.64	<0.12-5.3	BDE47: <0.03-0.70 BDE99: <0.03-0.90	<0.10	Kilemade et al., 2004
Riverine and marine sediments, Barcelona and Tarragona, Spain				0.86-2.49		de la Cal et al., 2003
Cinca River, Spain (2002)			n.d.-514	2.4-41.7		Eljarrat et al., 2004
3 Spanish Rivers (2012)				n.d.-812		Cristale et al., 2013
Remote lakes, Svalbard, Norway (2005)		0.18-13 (3.12)		0.05-0.61 (0.25)		Jiao et al., 2009
Near suspected sources, Norway				BDE-47: 0.04-6.1 BDE-99: n.d.-6.9	0.1-62	Nyholm et al., 2013
Scheldt basin, Belgium (2000)			<0.2-950 (60)			Morris et al., 2004
Western Scheldt (2000)			<0.6-99 (10)			
England (2000/2)			<2.4-1680 (199)			
North Sea Estuaries, Netherland (2000)			<0.8-9.9 (3.2)			
North Sea Estuaries, Dublin Bay, Ireland			<1.7-12 (3.3)			
Seine river basin, France		16-199		0.18-10.8	n.d.-297	Teil et al., 2014
13 estuarine sites around Auckland, New Zealand				0.55-573		Stewart et al., 2014
River Viskan, near a textile industry, Sweden			<0.1-25			Remberger et al., 2004

Description (Sampling Year/Year Range)	ΣPCBs	ΣHBCDs	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
11 isolated lakes, Sweden (2007)				Deca-BDEs: 0.48-11 (2.91)	Ricklund et al., 2010
Collected on the transect through the Stockholm archipelago (2008)				Deca-BDEs: 1-88 (18.9)	
River Elbe, Germany and the Czech Republic			0.5-17		Sawal et al., 2004
Belgian North Sea and the western Scheldt Estuary			<0.2	1.1-24	Voorspoels et al., 2004
Western Scheldt Estuary			<0.2 -18	1.5-1200	
Freshwater tributaries of River Scheldt			<0.2-19	<0.1-320	
Outside Europe					
Lake Superior (2001/2)	1.99-27.5 (3.6)		0.49-3.14 (1.43)	4.3-17.5 (10.5)	Song et al., 2004
Lake Michigan (2002)	18.3-41.7 (26.6)		1.67-3.97 (2.99)	43.9-95.6 (63.1)	Song et al., 2005b
Lake Huron (2002)	7.8-18.7 (11.4)		1.02-1.87 (1.51)	21.5-36.0 (28.8)	
Lake Erie (2002)	23.0; 28.3		1.95;1.83	55.4; 50.2	Song et al., 2005a
Lake Ontario (2002)	58.3; 63.6		6.33;4.85	211.2; 242.0	
Great Lakes (2007; Lake Superior, Michigan, Huron, Erie, and Ontario)		0.04-3.1		0.87-106	Yang et al., 2012
River areas, estuary, costal bays, Chile (2009)			BDE-47: n.d.-0.63 BDE-99: n.d.-0.83	n.d.-1.72	Barón et al., 2013
Intersection of Magdalena River and Caribbean Sea (2010)			BDE-47: n.d. BDE-99: n.d.	n.q.-143	
San Francisco Bay (2007)		0.1-1.7	2.1-8.0		Klosterhaus et al., 2012
Five mangrove swamps, Hong Kong			0.57-14.4	1.53-75.9	Zhu et al., 2014
Chinese streams near an e-waste recycling area (2006)		4.6-35 (14)			Zhang et al., 2009a
Donjiang River, industrialized region of South China (2006)			Σtri-hepta-BDEs: 0.7-7.6	Σnona-deca-BDEs: 30-5700	Zhang et al., 2009b
12 Chinese Lakes (2006)			0.02-0.29 (0.18)	0.11-40.1 (8.2)	Wu et al., 2012
Dongjiang River, Pearl River Delta, Southern China (2002/6)			2.60-60.4	32.7-2015	Shi et al., 2009

Description (Sampling Year/Year Range)	ΣPCBs	ΣHBCDs	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
Laizhou Bay area, China (2009; where the largest manufacturing base of BFRs in Asia is located)			Riverine: 0.01-53 (4.5) Marine: n.d.-0.66 (0.32)	Riverine: 0.74-285 (54) Marine: 0.66-12 (5.1)	Pan et al., 2011
Taihu Lake, China		0.046-2.56			Xu et al., 2013
River Tsurumi, Japan (2008)		0.8-4.8			Managaki et al., 2012
River Yodo, Japan (2008; populated area)		7.5-112			
River Kuzuryu, Japan (2008, source area)		134-2057			
Durban Bay and 13 rivers, South Africa (2011)		n.d.-27500 (1800) ng g^{-1} TOC	n.d.-7430 (423) ng g^{-1} TOC	n.d.-44500 (3208) ng g^{-1} TOC	La Guardia et al., 2013

As summarised in Table 4.5, concentrations of PCBs in surficial sediment layers from the sites monitored in this study covered a wide range, generally slightly lower than those detected in the Great Lakes, with concentrations at the more rural/remote sites comparable with those reported for Cork harbour, Ireland and remote lakes from Norway.

Concentrations of HBCDs and PBDEs in this study are consistent with those observed previously worldwide for surficial sediment layers from sites without obvious point sources (Song et al., 2004, 2005a, 2005b; Yang et al., 2012; Teil et al., 2014; Zhu et al., 2014); but were exceeded substantially by those from point source-impacted locations (Allchin et al., 1999; Managaki et al., 2012; Morris et al., 2004; Pan et al., 2011; Voorspoels et al., 2004; Stewart et al., 2014; La Guardia et al., 2013).

Table 4.6 Summary of concentrations (ng g^{-1} dw) of major NBFRs in surficial sediments (mean values in parentheses)

Description (Sampling Year/Year Range)		TBPH	DBDPE	BTBPE	TBBPA-DBPE	PBEB	Reference
Seven English Freshwater Lakes	***Top layer (2006-2011)***	***3.33-200 (61.6)***	***0.28-2.09 (0.76)***	***0.04-1.77 (0.47)***	***1.48-9.46 (3.91)***	***0.42-13.1 (3.33)***	***Current Study***
	Second layer (2001-2005)	***1.70-163 (45.8)***	***0.15-1.78 (0.49)***	***0.01-0.53 (0.22)***	***0.66-5.78 (2.96)***	***0.55-11.3 (3.04)***	
	Third layer (1995-2000)	***2.82-129 (37.3)***	***0.10-0.96 (0.33)***	***0.02-0.97 (0.25)***	***0.51-12.1 (3.31)***	***0.44-7.69 (3.63)***	
Europe							
11 isolated lakes, Sweden (2007)			0.23-11 (1.75)				Ricklund et al., 2010
Marine sediments, collected on the transect through the Stockholm archipelago (2008)			0.18-11 (2.78)				
Western Scheldt, Netherlands (2001)			24				Kierkegaard et al., 2004
Western Scheldt estuary, Netherlands (2005)			0.65-9.8	n.d.- 0.31			López et al., 2011
Metal recycling area, Norway (2009)						0.028	Arp et al., 2011
Other potential source zones, Norway (2009)						n.d.	
Near suspected sources, Norway			n.d.	n.d.-1.0	n.d.		Nyholm et al., 2013
Llobregat and Anoia River, Spain (2005/6)			4.8-24			n.d.-9.6	Guerra et al., 2010
Three rivers, Spain (2012)			n.d.-435	n.d.		n.d.	Cristale et al., 2013
Outside Europe							
River areas, estuary, coastal bays, Chile (2009)			n.d.-2.26			n.d.-0.15	Barón et al., 2013
Intersection of Magdalena River and Caribbean Sea, Colombia (2010)			n.d.			n.d.	
San Francisco Bay (2007)		<0.20	<24	<0.03-0.06		<0.03-0.1	Klosterhaus et al., 2012
Lake Michigan (2004)				close to 10			Hoh et al., 2005
Great Lakes (2007) (Lake Superior, Michigan, Huron, Erie, Ontario)			0.11-2.8	0.13-8.3			Yang et al., 2012
Lake Winnipeg, Canada (2002)				n.d.			Law et al., 2006
Durban Bay and 13 rivers in South Africa (2011)		n.d.- 899 (96) ng g^{-1} TOC	n.d.- 1840 (171) ng g^{-1} TOC	n.d.- 616 (34) ng g^{-1} TOC			La Guardia et al., 2013
12 Chinese Lakes (2006)			n.d.-3.64				Wu et al., 2012
Donjiang River, industrialised region of South China (2006)			19-430				Zhang et al., 2009b
Dongjiang River, Southern China (2002/6)			38.8-364	0.05-21.9	<1.5-2300		Shi et al., 2009

Regarding NBFRs, fewer comparisons could be made due to the comparative dearth of studies on NBFRs in sediments. The available data are summarised in Table 4.6. This shows that reports of TBPH concentrations in sediments are extremely rare. The non-detection of TBB and TBPH in San Francisco Bay sediments was attributed by the authors to matrix interferences (Klosterhaus et al., 2012). TBPH concentrations were found ranging between below detection limit to 899 (average=96) ng g^{-1} TOC in surficial sediment samples collected in 2011 from Durban Bay and 13 rivers in South Africa (La Guardia et al., 2013), with a comparable maximum TBPH concentration but a slightly lower average TBPH concentration than in our English lakes (8.95-609 ng g^{-1} TOC, average =238 ng g^{-1} TOC). This is the only comparable study on TBPH of which we are aware. Our concentrations of BTBPE in surficial sediment layers were comparable with or exceeded slightly those found in other European countries, but were at the lower end of those found in the Great Lakes and the Dongjiang River, South China, with average concentrations in surficial sediments across seven lakes being about two orders of magnitude lower than those from Durban Bay and 13 rivers in South Africa (La Guardia et al., 2013), while the concentrations of BTBPE in San Francisco Bay and Lake Winnipeg sediments (not detectable) were at the lower end of those found in this study. While concentrations of DBDPE in this study were at the lower end of those found in other European locations and China, and were generally comparable with those found in the US; they were about two orders of magnitude lower than those from Durban Bay and 13 rivers in South Africa (La Guardia et al., 2013). In other European studies, concentrations of PBEB were comparable with our data, but were detected less frequently. By comparison, PBEB concentrations in the US were exceeded by those in this study. Finally, while TBBPA-DBPE concentrations in our surficial lake sediments were at the very lower end of those found in South China, they exceed those reported in Norway.

4.6 Spatial Trends and Influencing Factors

Overall, the spatial distribution of our target compounds in English lake sediments were similar, regardless of which contamination metric was used - i.e. concentrations in surficial sediment layers, input fluxes, or inventories. The potential influence on contamination of parameters like lake depth, perimeter, surface area, catchment area, catchment ratio, and population density (both within the area covered by the unitary authority within which the lake is situated and within a 25 km radius of each site) was investigated. Due to the limited sample size, Spearman's rank

correlation coefficient (rho) rather than Pearson correlation coefficient was adapted for statistical analysis here.

For most target compounds, greatest contamination was consistently observed at either the MARM or EDGB sites, which have the lowest catchment ratios (both 0.1), and highest local population densities (both >2500 km^{-2}); while the lowest contamination was consistently detected at SLT and/or CRAZ, which possess both the highest catchment ratios (0.5 and 0.3 respectively) and the lowest local population densities (both only ≤100 km^{-2}). As confirmed by Spearman's rho coefficients (one-tailed significant level, see Table 4.7), the inventories of some contaminants were significantly correlated with local population density, and in some instances with the population density within a 25 km radius. Previously, Sun et al. (2007) reported a strong positive correlation between average atmospheric PCB concentrations near the Great Lakes and the local population within a 25 km radius of their sampling sites. Similarly, the concentrations of PBDEs, BTBPE, TBB, TBPH, and DBDPE were related to the number of people within a 25 km radius of the sampling site in a study on air and precipitation samples from North American (Ma et al., 2013). Moreover, Harrad and Hunter (2006) reported substantially higher airborne PBDE concentrations in urban locations along an urban-rural transect in the West Midlands of the UK. Given these observations, coupled with the abundant use of PBDEs in consumer goods and the greater prevalence of these in densely-populated areas, we believe the contamination by POPs in our lakes is clearly influenced by diffuse emissions related to the local population.

In contrast to the apparent lack of influence on POPs contamination of lake properties, e g., lake depth, lake perimeter, and lake area; significant negative linear correlation between lake catchment ratio and contamination level was observed for all legacy compounds and several of the frequently detected NBFRs (see Table 4.7). This indicates contamination to be elevated in lakes with surface areas that are small relative to their catchment area.

Statistically significant correlations between TOC content and POPs concentrations have been reported for, e.g., surficial sediments from the Daliao River Estuary (Zhao et al., 2011b), as well as for surface marine but not riverine sediments from the Layzhou Bay area (Pan et al., 2011). In this study, no such correlations were discernible. This is not surprising, given the influence of other parameters described above.

Table 4.7 Correlation coefficients and significance levels of relationships between POPs inventories and potentially influential parameters

Compounds	Local Population Density	Population Density within a 25 km Radius	Lake Catchment Ratio
ΣPCBs	0.918**		-0.767*
ΣHBCDs			-0.898**
Σtri-hexa-BDEs	0.863**		-0.898**
BDE-183	0.898**		-0.784*
BDE-209	0.973**	0.704*	-0.748*
TBPH	0.973**	0.704*	-0.748*
PBEB	0.973**		-0.692*
TBB	0.973**	0.778*	-0.692*
DBDPE	0.973**		-0.692*
TBBPA-DBPE	0.771*	0.815*	
BTBPE	0.954**		-0.680*
TBECH	0.954**		-0.680*
sDP	0.952**	0.769*	
ΣDP	0.962**	0.777*	
PBCC			-0.736*

* Significant at $p<0.05$ Level

** Significant at $p<0.01$ Level

4.7 Congener Patterns of POPs

4.7.1 PCB Congener Profile

Figure 4.6 (a) and (b) show the broadly equal relative abundance of the PCB congeners monitored in this study, with slightly higher abundance of PCBs 118 (16%), 153 (19%), and 138 (20%). The PCB congener pattern showed also no consistent temporal trend within sites. In contrast, lower chlorinated PCBs dominated in water samples in the same study (across the same 7 lakes, see details in Chapter Ⅲ), as shown in Figure 4.6. Moreover, in our English lakes, the relative abundance of all individual PCB congeners in surficial sediment samples were statistically significantly different to those in water samples (independent-samples t test, $p<0.05$ for PCB 101, and $p<0.001$ for all the remaining congeners).

To further investigate, as illustrated in Figure 4.7, the ratios of the relative abundance of all individual PCB congeners in surficial sediment (expressed as a percentage of ΣPCBs) to those in water samples from the same lakes (average values from all 13 sample batches were used for each site) showed positive linear correlation with log K_{OW} values ($R=0.902$, $p<0.001$). This is plausible as higher log K_{OW} values will enhance the potential for partitioning to sediment relative to water.

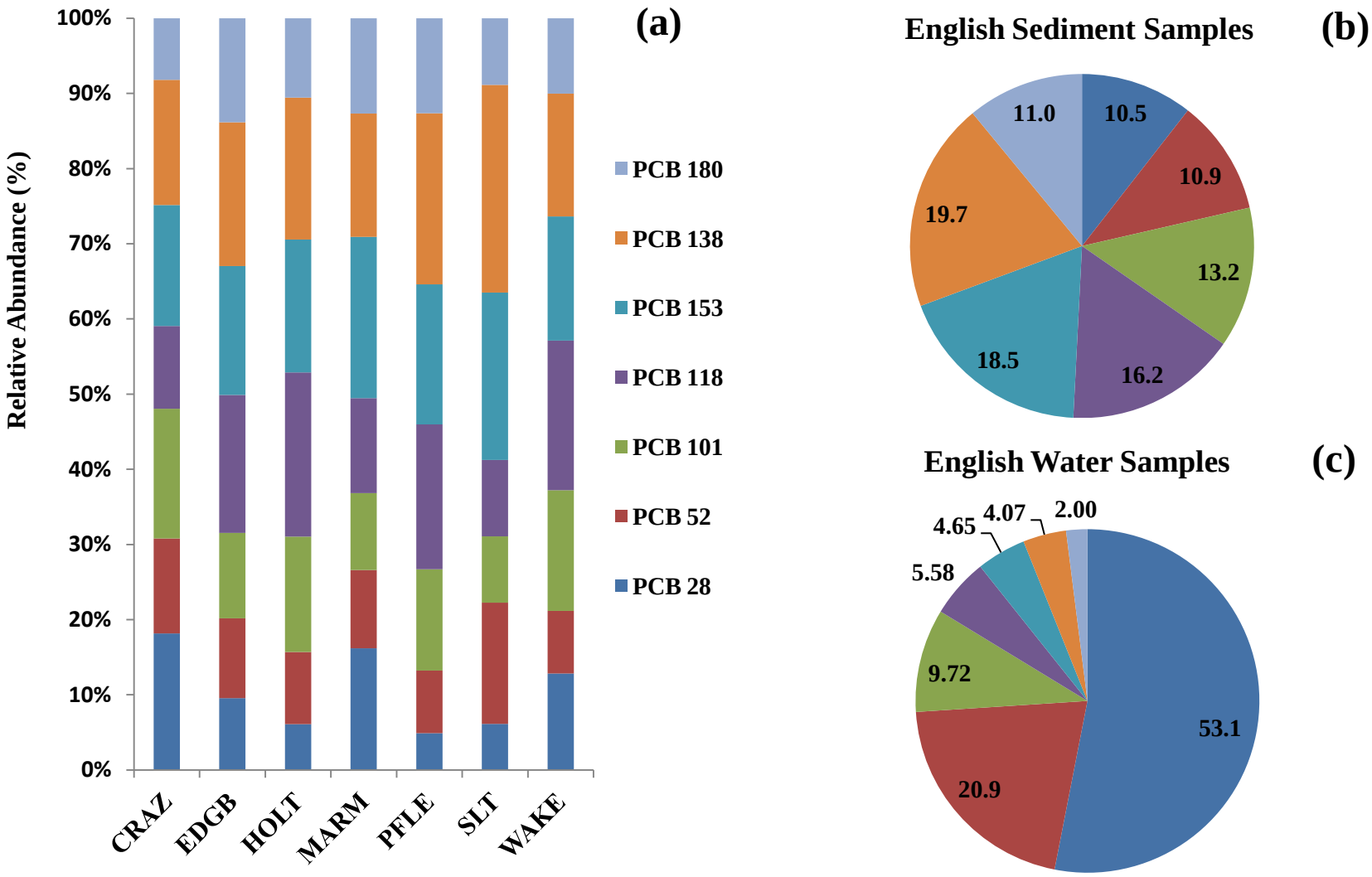


Figure 4.6 PCB congener profiles in sediment cores from seven English lakes, ~1950-2011/2 - (a) individual site averages, and (b) overall averages, and (c) in water samples from the same lakes (overall average)

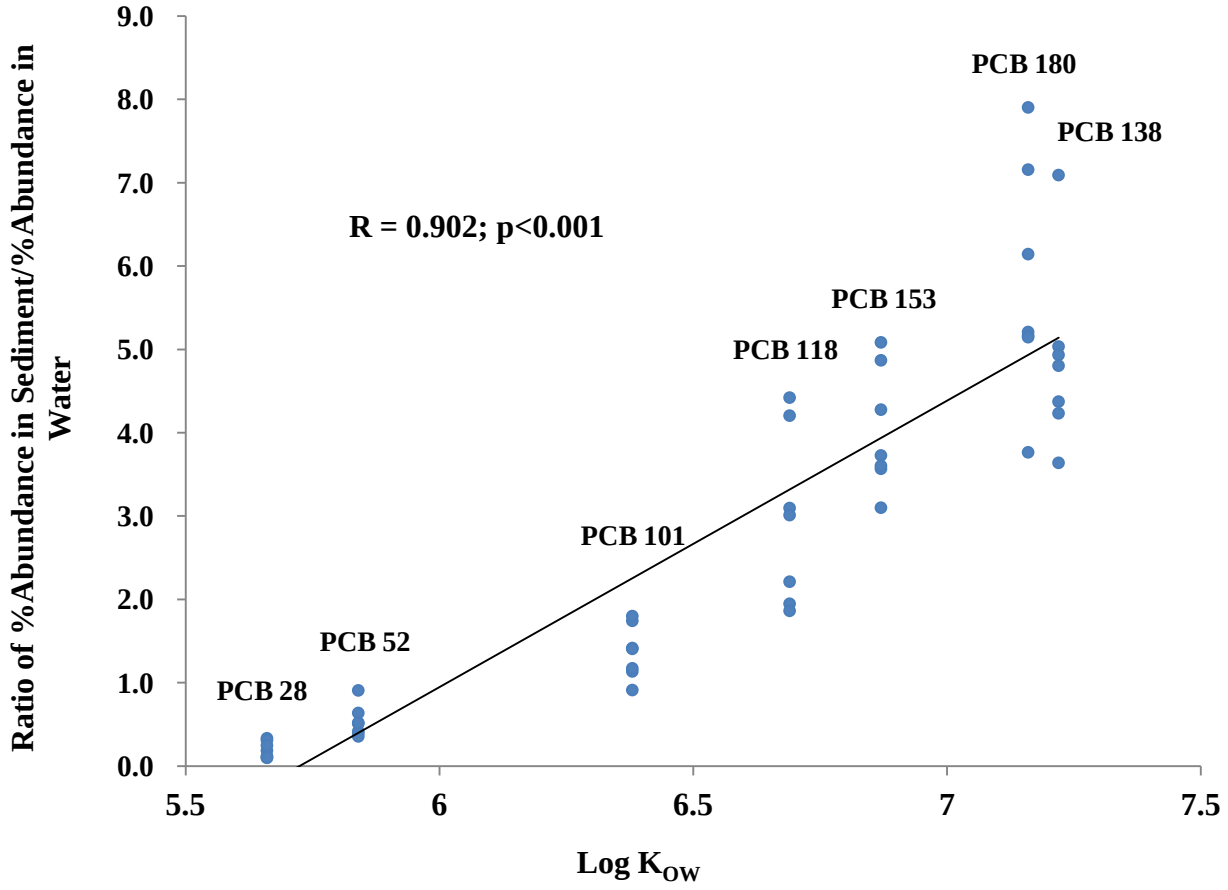


Figure 4.7 Relationship between Log K_{OW} and the ratio of relative abundance of individual PCB congeners in sediment to that in water

4.7.2 PBDE Congener Profiles

4.7.2.1 Discussion of PBDE Congener Pattern

As illustrated in Figure 4.8, the relative contribution of BDE-209 to ΣBDE concentrations in all 72 sediment samples in which it was detected ranged from 0.33 to 0.99, with mean and median values of 0.89 and 0.93, respectively. The average contributions of BDE-209 at EDGB, MARM, PFLE, SLT, and WAKE (≥0.92) were statistically significantly higher than those at CRAZ and HOLT (0.63, and 0.78, respectively) (ANOVA, $p<0.001$). Likewise, while Σtri-hexa-BDEs contributed 0.0-0.14 ΣBDEs at EDGB, MARM, PFLE, SLT, and WAKE; significantly greater contributions were detected at HOLT and CRAZ (0-0.34 and 0-0.67, respectively; ANOVA,

$p<0.001$). Such variations in the relative abundances of congeners representing the Penta-BDE and Deca-BDE formulations may suggest spatial variation in inputs of these formulations (e.g. generally higher abundance of Deca-BDE at EDGB, MARM, PFLE, SLT, and WAKE than at CRAZ and HOLT). Alternatively (or perhaps additionally), these spatial differences in PBDE pattern may be attributable to differences between the environmental fate and behaviour of PBDEs associated with the Penta-BDE and Deca-BDE formulations. For example, the lower capacity of BDE-209 to undergo long-range atmospheric transport seems consistent with its lower relative abundance at more remote/rural sites like CRAZ and - to a lesser extent - HOLT. As a caveat to this general observation though, the local population density of the SLT site is in line with that of CRAZ; thereby indicating the observed congener patterns at each site is an integral of more than one factor.

With respect to temporal changes in PBDE patterns, it is apparent that BDE-209 has consistently been the predominant congener in English lake sediments since its emergence, but the extent of its dominance has fluctuated. The contribution of BDE-209 decreased from around 1960 reaching its lowest in the 1980s at most sites. This appears less because of a decline in Deca-BDE use at that point, but rather due to the emergence of congeners associated with Penta-BDE and Octa-BDE commercial formulae.

Consistent with our study, the predominance of BDE-209 over other BDE congeners was also observed in sediments from the Seine River basin (Teil et al., 2014), 13 estuarine sites in New Zealand (Stewart et al., 2014), five mangrove swamps in Hong Kong (Zhu et al., 2014), the Clyde Estuary in the UK (Vane et al., 2010), the Cinca River in Spain (Eljarrat et al., 2004), the Lake Maggiore basin (Italy and Switzerland; Guzzella et al., 2008), the River Elbe in Germany and the Czech Republic (Sawal et al., 2004), Durban Bay and 13 rivers in South Africa (La Guardia et al., 2013), riverine and marine sediments from Laizhou Bay area, China (Pan et al., 2011), as well as UK domestic indoor dusts (Harrad et al., 2008a, 2008b), to name just a few.

In our sediment core samples, BDE-99 exceeded BDE-47 in 39 out of 55 samples in which the former was detected. For comparison, the proportion of BDE-99 was greater than or equal to that of BDE-47 in 49 out of 71 sediment core slices from the inner Clyde Estuary in the UK (Vane et al., 2010). BDE-99 and BDE-47 were present at median values of 2.7 and 2.0% of ΣBDEs (BDE-209 included) in surficial sediments from 13 estuarine sites in New Zealand (Stewart et al.,

2014). More BDE-99 than BDE-47 was present in surficial sediment from five mangrove swamps in Hong Kong (Zhu et al., 2014). Furthermore, a similar excess of BDE-99 over -47 was found in 2 out of 3 sediment cores (Chen et al., 2007) and in all 33 surface sediments (Mai et al., 2005) analysed in studies of the Pearl River Estuary, China. In the Great Lakes, Song et al. (2004, 2005a, 2005b) reported BDE-47 to exceed BDE-99 in 62% of Lake Superior sediment core samples collected between 2001 and 2002, with a similar pattern detected in sediments from Lakes Michigan, Huron, and Ontario in 2002. In contrast, the contribution of BDE-47 was slightly lower than that of BDE-99 in Lake Erie sediment in 2002; while the BDE-47:99 ratio estimated based on the data of Dodder et al., (2002) was only 0.5 for Lake Hadley, IN (Song et al., 2004). The evidence from the various studies conducted in the Great Lakes is therefore consistent with the variable patterns observed in this study, whereby BDE-99 exceeds BDE-47 in many samples, but with the reverse observed in a significant minority of sediment samples. Our observations are also indicative of a slight "weathering" of the BDE-47:99 ratio present in the Penta-BDE commercial formulation. Specifically, two technical Penta-BDE mixtures, Bromkal DE-71 and 70-5DE, contained 49% and 45% BDE-99, and 38% and 43% BDE-47, respectively (La Guardia et al., 2006).

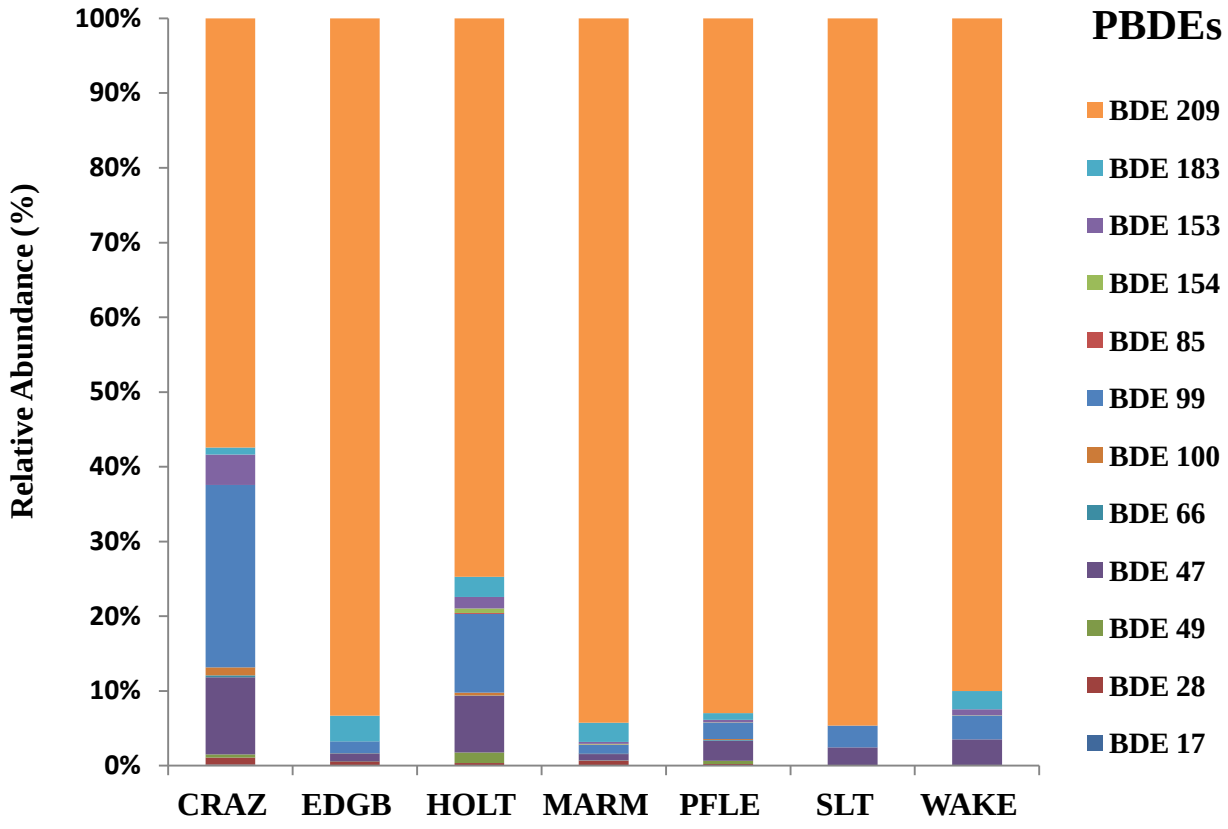


Figure 4.8 PBDE congener profiles (individual site averages) in sediment cores from seven English lakes, ~1950-2011/2

4.7.2.2 Temporal and Spatial Trends in Ratios of BDE-47:99

As shown in Figure 4.9, while BDE-47:99 ratios showed no consistent temporal trends across our seven studied lakes, statistically significant spatial variations were observed (ANOVA, $p<0.001$). To further investigate, with the removal of an apparent outlier- the highest concentration found in surficial sediment from EDGB, the ratio of BDE47:99 over all samples were found moderately correlated with Σtri-hexa-BDE concentrations (on TOC normalised basis; $R=0.236$, $p=0.086$). Combined with the observation that relatively higher Σtri-hexa-BDE levels were found at urban sites while lower concentrations were found in rural/remote sites that are further away from emissions, we therefore hypothesis that BDE-99 is more persistent and capable of environmental transport than BDE-47, which could lead to the BDE47:99 ratio shifts towards BDE-99 when reach more remote locations. Moreover, the suggestive but not conclusive link between

BDE47:99 and Σtri-hexa-BDE concentrations indicating likely other influencing factors on BDE47:99 as well as distance from emission source(s).

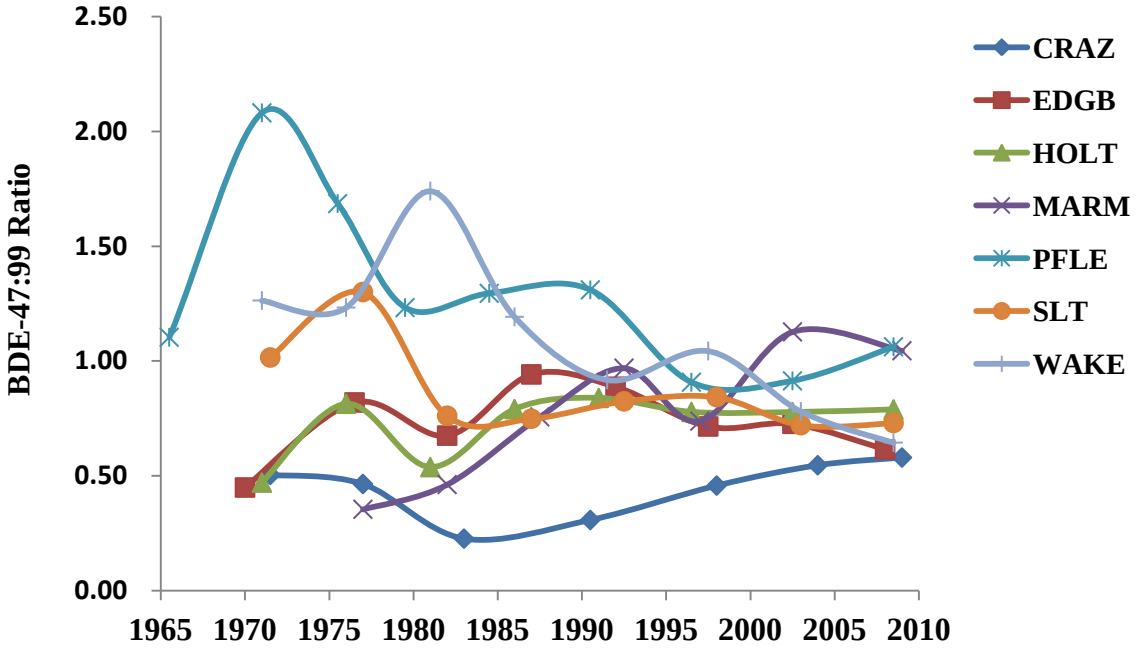


Figure 4.9 Historical changes in BDE-47:99 ratios in lake sediment core slices

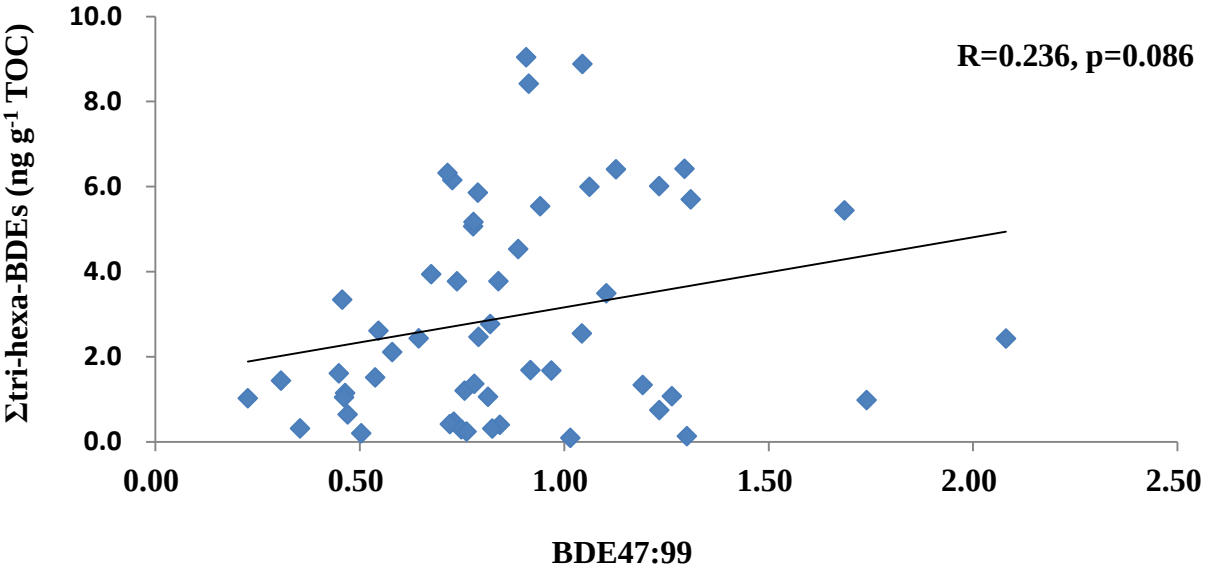


Figure 4.10 Correlation between ratios of BDE47:99 and Σtri-hexa-BDE concentrations (TSS normalised basis)

4.7.2.3 Comparison of PBDE Congener Profiles in Sediments vs. Bulk Water

The BDE-47:99 ratios in our sediment core samples and in water samples from our previous study from the same seven English lakes ranged from 0.23 to 2.08, and 0.38 to 3.89, respectively, with similar mean (0.86 and 1.04, respectively) and median values (0.79 and 0.83 respectively). When each site is examined individually, BDE-47:99 ratios in sediment cores were lower than in water at CRAZ, but higher at PFLE ($p<0.01$, and 0.05, respectively; two-tailed; independent t-test), with sediment and water ratios statistically indistinguishable at all other lakes studied. Moreover, principal component analysis (PCA) showed no clear difference between PBDE congener profiles of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153 in sediment cores and bulk water.

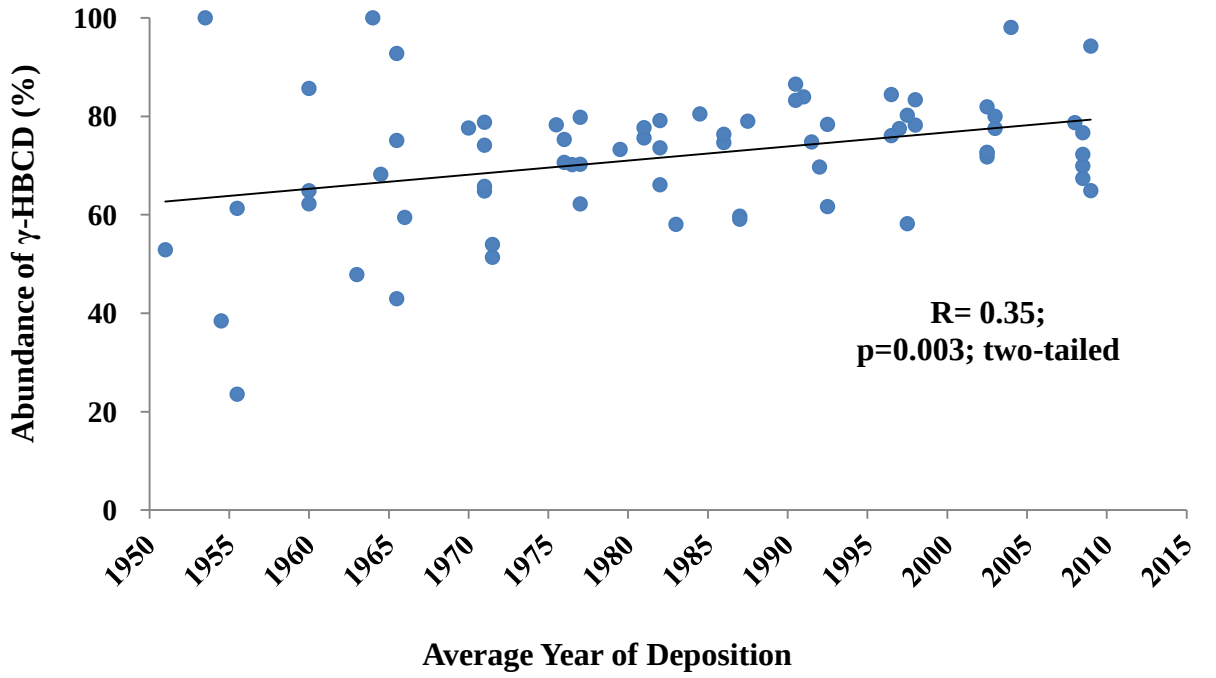
BDE-47:99 ratios across all sites showed no statistically significant correlation with potentially influential factors, e.g., dry mass content, and average year of sedimentation of sample. However, a statistically significant negative correlation between BDE-47:99 ratios and TOC content was observed (R=0.36). Also strikingly, the correlation with the ratio of TOC/dry mass was highly significant (R=0.48). This observation is likely due to the greater hydrophobicity of BDE-99 than BDE-47 indicated by the higher K_{OW} of the former (Palm et al., 2002).

4.7.3 Influencing Factors on HBCD Isomeric Profiles

The contributions of α- and γ- to ΣHBCDs in this study ranged from zero (i.e. not detected) to 0.51 (α-HBCD), and 0.24 to 1.0 (γ-HBCD), with mean (median) values of 0.18 (0.17), and 0.72 (0.74), respectively, in 70 out of the 74 sediment core samples analysed where at least one of the two isomers were detected. β-HBCD consistently displayed the lowest contribution to ΣHBCDs. The stereoisomeric profile of HBCD in English freshwater lakes was consistent with those observed in sediment from Taihu Lake, China (Xu et al., 2013), Japanese river sediments (Managaki et al., 2012), Cinca River sediment (Spain; Guerra et al., 2009), most sediments in a study of western European estuaries including the Netherlands, Dublin Bay in Ireland, the Scheldt basin in Belgium, the Western Scheldt, and the UK (Morris et al., 2004), sediments from streams in China (Zhang et al., 2009a), and most riverine and estuarine sediments at various sites throughout the UK (Morris et al., 2004). In all of these cited studies, the profile was dominated by γ-HBCD, thereby closely resembling that for the commercial HBCD formulation (10-13% α-, and 75-89% γ-HBCD, respectively; Becher 2005).

Consistent with an earlier study from our group (Harrad et al., 2009) in which δ-HBCD was found in fish, but not in water and surface sediments from the same English freshwater lakes as in the current study; no δ-HBCD was detected in any of our sediment core samples.

Relevant parameters that may affect HBCD isomeric profiles were investigated carefully across all sites in this study (see Figure 4.11). Interestingly, the contribution of γ- to ΣHBCDs (i.e. its relative abundance) increased significantly ($R=0.35$, $p=0.003$) with increasing year of deposition, and was greater at higher HBCD concentrations (on both dry sediment material and TOC basis). The increased relative abundance of γ-HBCD in more recently sedimented material is consistent with fresher input of HBCD in view of the fact that the commercial product is predominantly γ-HBCD. A similar rationale may also account for the higher predominance of γ-HBCD at higher ΣHBCD concentrations, based on the premise that higher concentrations of HBCD are more likely associated with "fresher" inputs. It could also be due to within-core, post-depositional isomerisation favouring α-HBCD formation in older sedimented material.



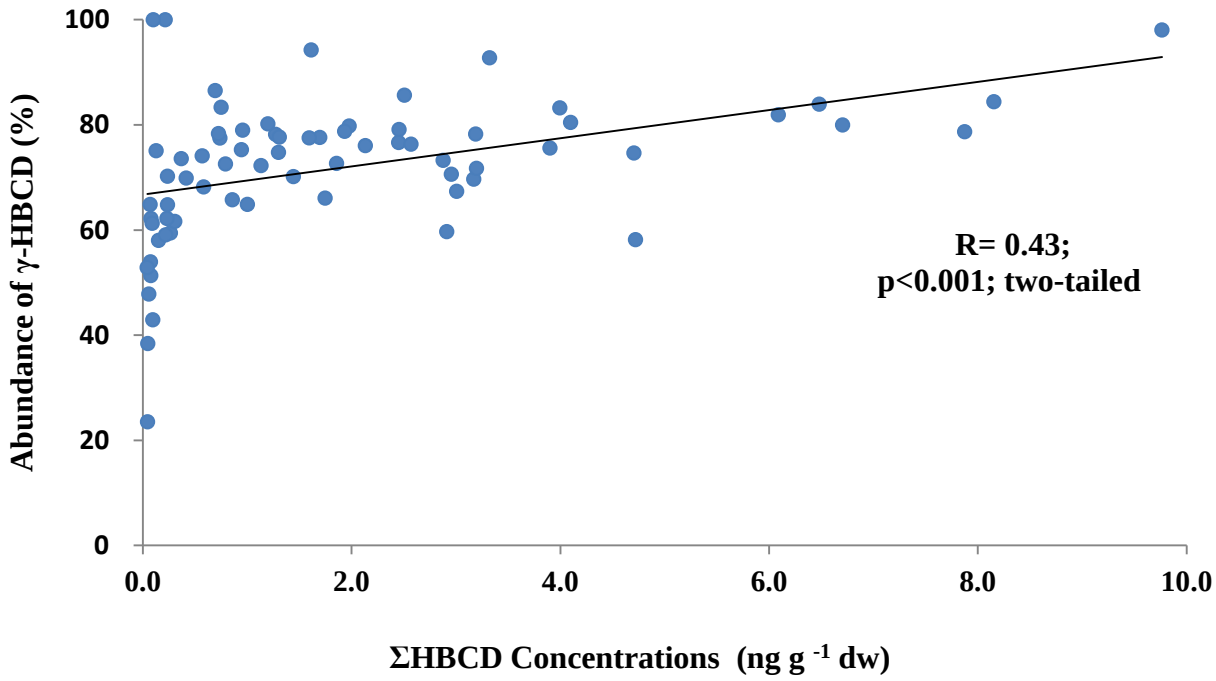


Figure 4.11 Correlation between ratios of γ- HBCD relative to ΣHBCDs and (top) average year of deposition and (bottom) ΣHBCD concentration (ng g^{-1} dw)

4.7.4 NBFRs

TBB and TBPH are two of the active ingredients of the commercial flame retardant product Firemaster 550 (FM 550), which was introduced in 2003 as an alternative to the Penta-BDE commercial formula (Stapleton et al., 2008). FM 550 also contains isopropylated triaryl phosphate, and triphenyl phosphate (Chemtura, 2006). In this study, the ratio of TBB:TBPH in surficial sediment samples across all sites ranged from 0.01 to 0.06, with an average of 0.02. This is significantly lower than the ratio of approximately 3:1 (Ma et al., 2013) and 4:1 (Stapleton et al., 2008) in commercial FM 550. The average TBB:TBPH ratio detected in sediments from Durban Bay and 13 rivers in South Africa was 5.7 (La Guardia et al., 2013), which is in distinct contrast to our observations in English lakes. In other studies, TBB:TBPH ratios ranged from 0.01 to 4.77 (average 0.42) in Belgian and UK indoor dust (Ali et al., 2011a), 0.02 to 0.27 (average 0.08) in indoor dust from e-waste recycling facilities in Thailand (Ali et al., 2011b) and 0.0003 to 3 in blubber of Indo-Pacific humpback dolphins and finless porpoises (Lam et al., 2009), and were on average 0.82 in North American outdoor air (Ma et al., 2013). Hence our TBB:TBPH ratios were at the lower end of values reported for a range of environmental matrices, which likely results from the likely more extensive application of TBPH than TBB in the UK, as well as reflecting variable distribution of TBB and TBPH in different environmental compartments due to their physicochemical properties. Moreover, the significant disparity between the ratios in our study suggests strongly that FM 550 is only a minor source of TBPH in the UK environment. In contrast, the less marked discrepancy between the TBB:TBPH ratio in North American outdoor air (Ma et al., 2013) and that observed in FM 550, suggests that while other sources of TBPH exist also in North America, use of FM 550 (likely in furniture foam) is substantial in that region.

Chapter Ⅴ

Temporal Trends of HBCD Concentrations in Suspended Sediments from Niagara River in Canada, 1980-2012 - A Case Study for Comparison with English Lakes

5.1 Introduction

The Niagara River flows north from Lake Erie to Lake Ontario, forming part of the border between the Province of Ontario in Canada and New York State in the US. It is the primary watercourse discharging to Lake Ontario, contributing approximately 85% of the total input, and roughly half of the fine-grained sediments entering the lake (Kemp and Harper, 1976). The Niagara River is of concern due to its severe environmental degradation, and was thus listed as a Great Lakes Area of Concern in 1987 under the Great Lakes Water Quality Agreement between the US and Canada (Niagara River Area of Concern, 2010).

Archived suspended sediment samples collected over the period 1980-2012 at Niagara-on-the-Lake station, which is at the mouth of the Niagara River in Lake Ontario at the Canadian side, were analysed to assess temporal trends in contamination by HBCDs. Monitoring temporal trends in HBCD contamination at the outlet of the Niagara River enhances understanding of historical changes in HBCD inputs into the river and its discharge of HBCDs to Lake Ontario, reflecting also the historical changes in discharges of HBCDs from regional population centres along the watershed. Samples taken in spring and summer of the period 2004-2012 were used to assess seasonal trends of HBCDs in the Niagara River. The observed temporal trends in concentrations of HBCDs in the Niagara River will be compared with our observations in English freshwater lakes.

5.2 Experimental Section

Details of sampling locations and strategies, sample preparation, analytical methods, instrumental analysis, and QA/QC are described in the methodology chapter (ChapterⅡ).

5.3 HBCDs in Niagara River Suspended Sediments

5.3.1 Temporal Trends of HBCDs over the Last 33 Years

In total, 39 suspended sediment samples were analysed. To be specific, one sample was analysed for each year during 1980~2003, except for 2000 where no archived sample extract was available; with one to two samples analysed for each year over the period of 2004 to 2012 inclusive.

Figure 5.1 (a) shows that concentrations of HBCDs on both a water volume and TSS content normalised basis in Niagara River increased with fluctuations from the first monitored year of 1980, peaking in the late-1980s and early 1990s, respectively, before declining generally thereafter with some fluctuations. HBCDs have decreased to extremely low levels from 2002 onwards, with also low detection frequency (47%). Suspended sediments from the Niagara River with HBCDs found above detection limits were used for calculation of the half-life time ($T_{1/2}$). The estimated $T_{1/2}$ was 4.4 years (1989-2012) and 5.1 years (1993-2012) for HBCD concentrations on a water volume and TSS content normalised basis, respectively. For comparison, as shown in Figure 5.1 (b), temporal trends of HBCD levels revealed by archived suspended sediments from the Niagara River were comparable with our observations from most of the English lakes studied in chapter Ⅳ, in which HBCD concentrations have declined or levelled-off from the early 2000s onwards. The one exception is at the most contaminated English lake (EDGB), where HBCD contamination increased throughout the monitored period and has showed no sign yet of decreasing or levelling off.

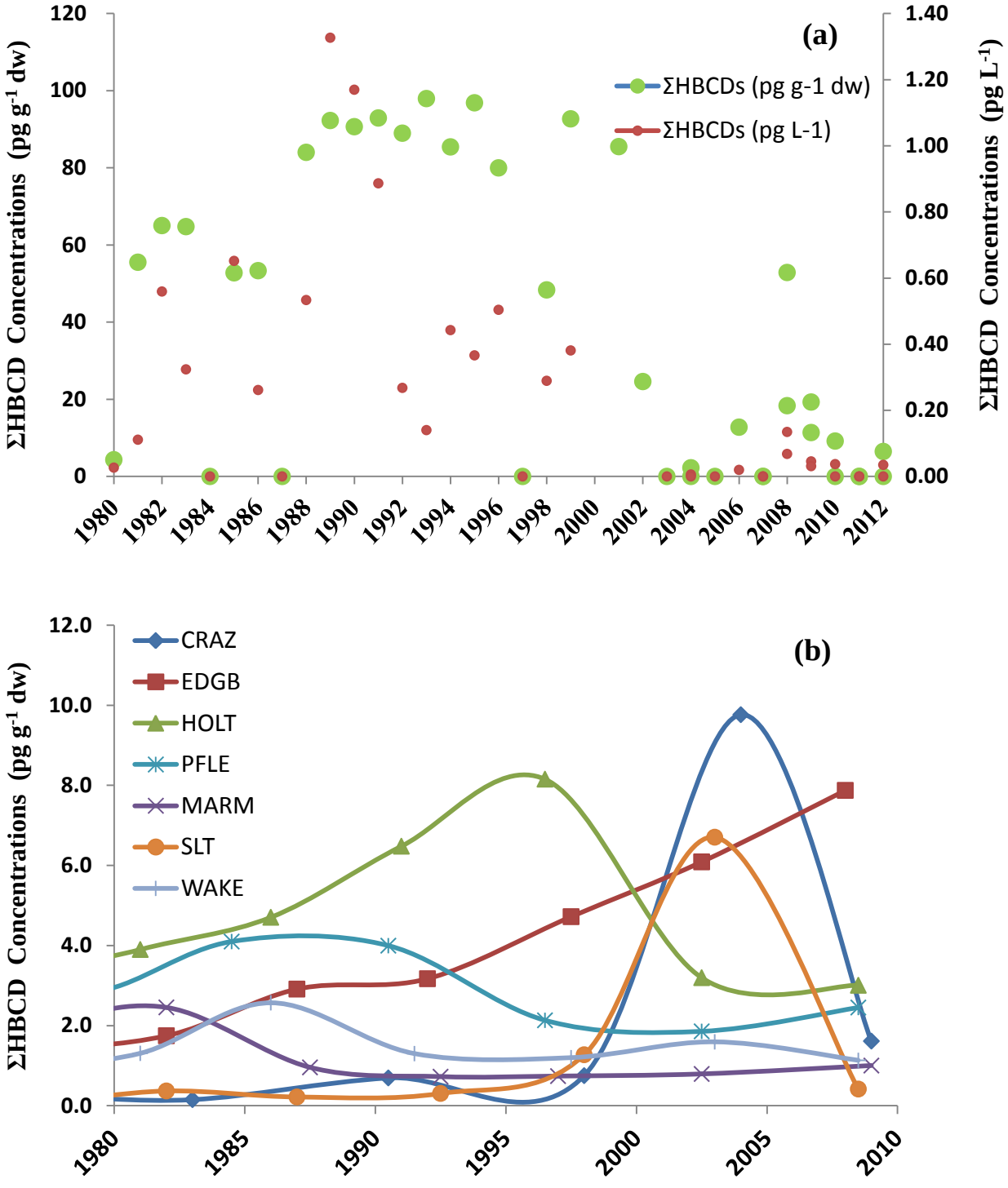


Figure 5.1 Temporal trends of ΣHBCDs in (a) archived suspended sediment samples from the Niagara River, 1980-2012, and (b) sediment cores from seven English freshwater lakes, 1980-2011/2

5.3.2 Seasonal Trends of HBCDs during March 2003 and August 2012

As shown in Figure 5.2, among the 16 suspended sediment samples collected in the spring and summer seasons during 2003 and 2012 for seasonal trend assessment; ΣHBCDs were relatively more frequently detected in samples taken in spring (5 out of 8 samples) than in those taken in summer (3 out of 8 samples). However, while average concentrations of ΣHBCDs expressed on a water volume normalised basis were very similar in spring (0.024 pg L^{-1}) and summer (0.023 pg L^{-1}); TSS normalised concentrations were lower in spring (6.94 pg g^{-1}) than in summer (9.63 pg g^{-1}), but with no statistical significance observed (t-test, $p>0.05$). For comparison, as shown in Figure 5.3, between July 2008 to February 2012, higher average concentrations of ΣHBCDs (expressed on both a water volume and TSS content basis) in colder than warmer periods were observed at most (but not all) studied English lakes. Note that in our study of English lakes, both operationally defined dissolved and particulate phases were analysed for HBCDs; while for Niagara River, only suspended sediments, similar to our operationally defined particulate phase, were analysed for HBCDs.

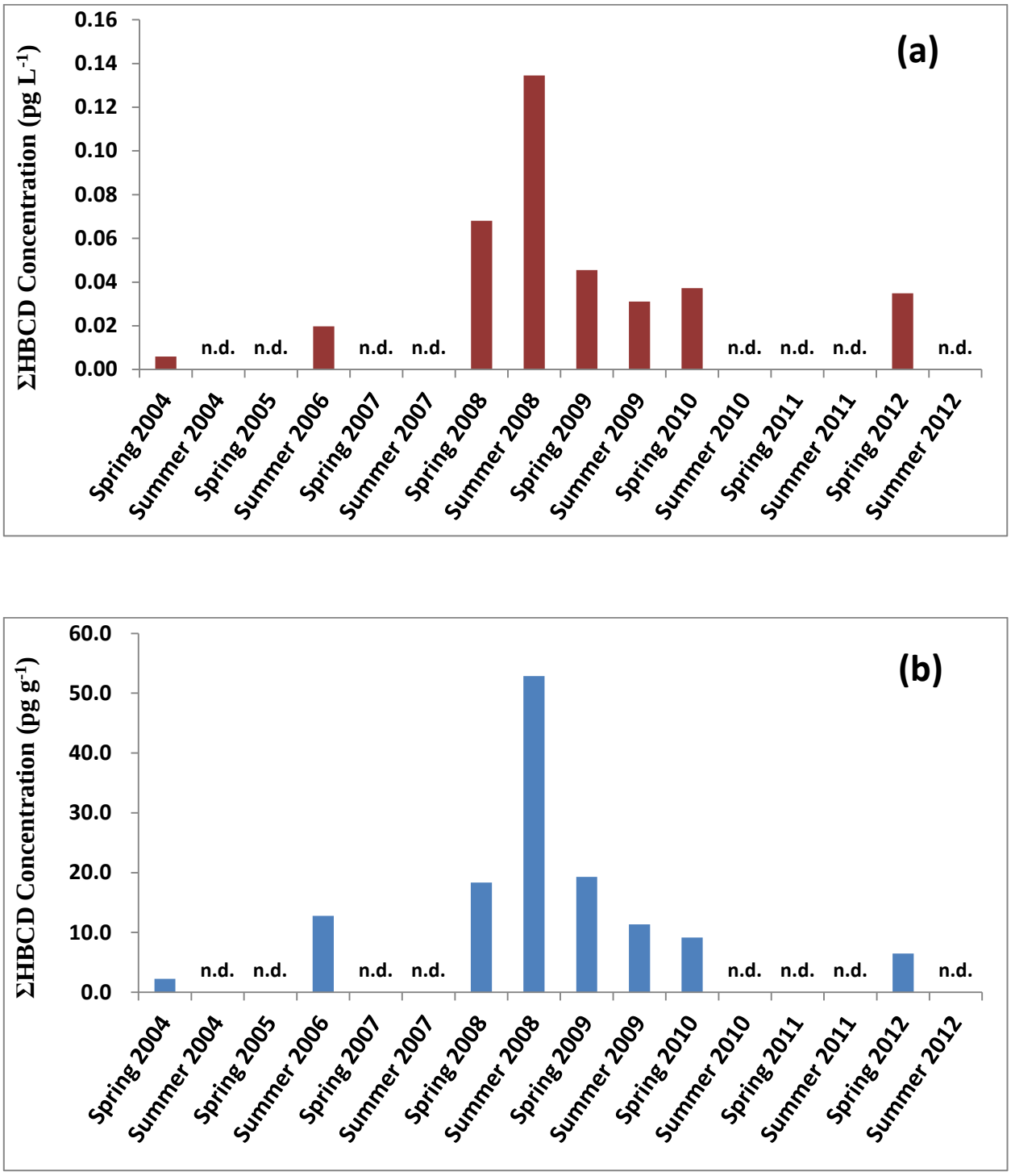


Figure 5.2 Seasonal trends in concentrations of ΣHBCDs in Niagara River suspended sediment on both: (a) a water volume (pg L^{-1}), and (b) TSS normalised basis (pg g^{-1} dw), spring 2004 to summer 2012

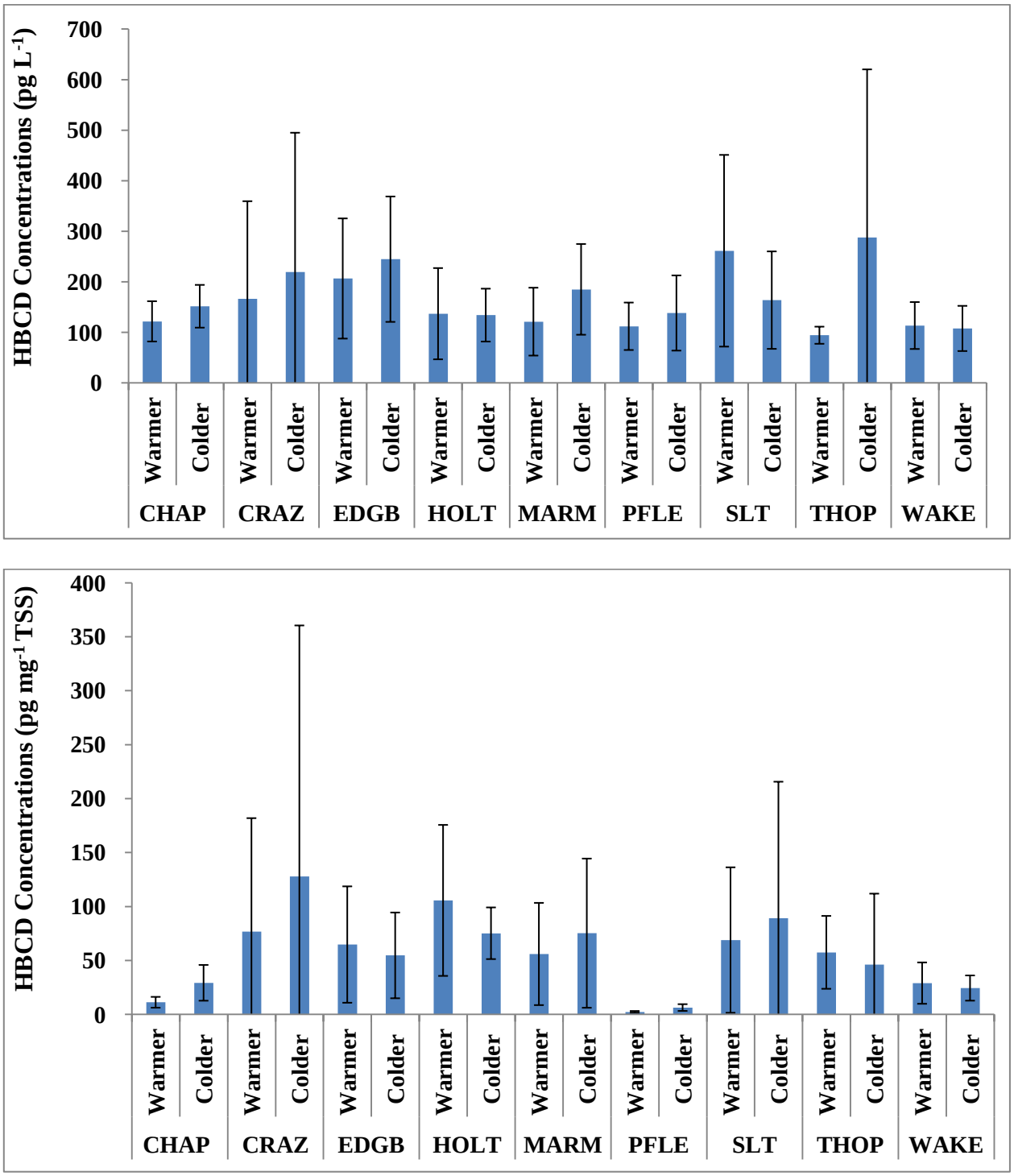


Figure 5.3 Seasonal trends in intra-site average concentrations of ΣHBCDs in water samples (sum of both phases) from English lakes on both: (a) a water volume (pg L^{-1}), and (b) TSS normalised basis (pg mg^{-1} TSS), July 2008 to February 2012

5.3.3 HBCD Concentrations in Suspended Sediment from the Niagara River

HBCDs were detected above the detection limit in 27 out of 39 archived suspended sediment samples from the Niagara River during 1980 and 2012, with relatively higher detection frequency (86%) of HBCDs in samples collected prior to 2002 inclusive, see Table 5.1 for details of samples with HBCD found above quantification limit. The maximum ΣHBCD concentration was 1.33 (mean=0.23, median=0.05 across all samples) pg L^{-1}, or 97.9 (mean=38.2, median=19.3 across all samples) pg g^{-1} dw on a TSS normalised basis. Note that suspended sediments represent only the particulate phase in bulk water. Given that in English lake water, 47-61% (mean=53%) of ΣHBCDs were found in the particulate phase, concentrations of ΣHBCDs in Niagara River bulk water were estimated to be about twice that in its suspended sediments. Even allowing for this, concentrations of ΣHBCDs (combined dissolved and particulate phases) in water samples from 9 English lakes ranging from 45 to 890 (mean=165) pg L^{-1} or 1.4 to 600 (mean=56) ng g^{-1} dw during 2008 and 2012 were about 3 orders of magnitude higher than those detected in the Niagara River. With respect to English sediment core samples, after its first emergence, ΣHBCD concentrations (0.06-9.76 ng g^{-1} dw) was consistently found above detection limits in English sediment core segments, with mean and median values of 2.02 and 1.30 ng g^{-1} dw, respectively. This is approximately two orders of magnitude higher than HBCD levels recorded in our archived Niagara River suspended sediment samples. The observation of lower HBCD concentrations in the Niagara River is plausible given that in 2001, 60% of the commercial HBCD was consumed in Europe compared to 17% in the Americas (BSEF, 2006), indicating potentially more HBCD could have been released into the European than North American environment. Moreover, HBCD concentrations in North America could be further "diluted" due to the lower population density than in European countries like the UK. Interestingly however, concentrations of ΣHBCDs in surficial sediments collected in 2007 from the Great Lakes (0.04-3.1 ng g^{-1} dw in Lakes Superior, Michigan, Huron, Erie, and Ontario) (Yang et al., 2012) are only a few times lower than those recorded in our surficial sediments from English lakes (0.42-7.87 ng g^{-1} dw).

5.3.4 Isomeric Profile of HBCDs in Niagara River Suspended Sediments

Overall, γ-HBCD was the dominant isomer, with an average relative abundance of 58% ΣHBCDs across all samples in which HBCD was detected. Interestingly, while γ-HBCD dominated in all

samples collected prior to 2002 inclusive with a relative abundance ranging between 13-100% ΣHBCDs (mean=73%); the equivalent values were 3.5-37% (mean=23%) for samples collected from 2003 onwards. One possible reason for this distinct change (t-test, $p<0.001$) is as follows: post 2002, fresh inputs of HBCDs (in which γ-HBCD dominated) to the Niagara effectively stopped, resulting in a shift in the diastereomer pattern towards a weathered one in which α-HBCD dominates. This is supported by the significant decrease in ΣHBCD concentrations post-2002.

Table 5.1 Concentrations[a] of ΣHBCDs in suspended sediments expressed on both a water volume (pg L^{-1}) and dry mass (pg g^{-1} dw) normalised basis, with relative abundance of γ-HBCD given

Sampling Year	Concentrations (pg g^{-1} dw)	Concentrations (pg L^{-1})	γ-HBCD Abundance (% ΣHBCDs)
1980	4.32	0.03	100
1981	55.5	0.11	70
1982	65.0	0.56	66
1983	64.8	0.32	81
1985	52.8	0.65	67
1986	53.3	0.26	70
1988	84.0	0.53	71
1989	92.3	1.33	79
1990	90.7	1.17	80
1991	92.9	0.89	73
1992	89.0	0.27	81
1993	97.9	0.14	79
1994	85.4	0.44	78
1995	96.9	0.37	80
1996	80.0	0.50	78
1998	48.4	0.29	13
1999	92.7	0.38	78
2001	85.5	-[b]	78
2002	24.6	-[b]	58
2004	2.24	0.01	27
2006	12.8	0.02	22
2008	18.3	0.07	3.5
2008	52.9	0.13	37
2009	19.3	0.05	24
2009	11.4	0.03	24
2010	9.17	0.04	18
2012	6.46	0.03	26

[a] HBCD concentrations were taken as zero where no HBCD isomer was found above detection limits. [b] Missing data on water volume

Chapter VI

Summary and Conclusions

6.1 Summary and Conclusions

The aims of the thesis were achieved with the main outcomes summarised below:

6.1.1 Lacustrine Water Samples, England

- Water samples taken from nine English freshwater lakes from a mix of urban, rural, and remote locations on 13 occasions between April 2008 and February 2012 were analysed for selected non-dioxin like- PCBs (40-390 pg L^{-1}, n=116), tri- through hexa-BDEs (9.2-170 pg L^{-1}, n=115), and the three main α-, β-, and γ-HBCD (45-890 pg L^{-1}, n=107), with detection frequency of 100% for all monitored POPs.

- PCBs and HBCDs were generally equally separated in the freely dissolved and particulate phases in bulk water, while a higher proportion of ΣBDEs (63-77%, mean=68%) was found in the particulate phase.

- Concentrations of both PCBs and PBDEs showed TSS dependence.

- TSS content (mean values), and PBDE and HBCD concentrations displayed seasonal trends, with higher values found in colder compared to warmer periods at 5 sites.

- Across all samples, linear regression analysis showed statistically significant decreasing trends in ln(PCBs) ($R=-0.429$, $p<0.001$, $T_{1/2}$ =3.8 years), and ln(HBCDs) ($R=-0.24$, $p=0.006$, $T_{1/2}$ =5.1 years) over the monitoring period.

- Statistically significant inter-site variability was observed for monitored POPs.

- Lower chlorinated PCBs were dominant in water. The major BDE congeners were BDE-99 and BDE-47. γ-HBCD was the principal HBCD isomer.

- BDE-47:99 ratios decreased with increasing TSS content, and displayed seasonal trends across all sites, with significantly higher ratios in warmer than colder periods ($p<0.01$). This is further confirmed by linear regression that shows BDE-47:99 ratios are significantly

influenced by season (higher in warmer months; $R=0.279$, $p<0.01$) and water temperature ($R=0.261$, $p<0.01$).

6.1.2 Lacustrine Sediment Cores, England

- Concentrations of PCBs, HBCDs, tri- through deca-BDEs, and 32 selected NBFRs were measured in radiometrically-dated sediment core slices taken in summer 2011/2 from seven of the same English lakes.
- Spatial variation in POPs contamination of the lakes studied was evident; with regression analysis suggesting concentrations are higher in lakes with surface areas that are small relative to their catchment area, and that are closer to areas of high population density.
- While our data show the continuing long-term legacy of past PCB use, it suggests a relatively rapid response to recent curbs on the use of Penta-BDE and HBCD, the continuing extensive use of Deca-BDE, and the rising use of some NBFRs; in particular TBPH.
- The estimated PCB burden in the British environment is 521 t, with TBPH (281 t) and BDE-209 (147 t) following not far behind. Estimated UK burdens of the remaining target compounds were significantly lower.
- In surficial sediment it is striking that TBPH was the dominant contaminant, while BDE-209 concentrations at two sites are in line with the highest historical PCB concentration.
- In this study, no significant correlations between TOC content and POPs concentrations were discernible, indicating stronger influences of other parameters such as those described above.
- PCBs 118 (16%), 153 (19%), and 138 (20%) showed relatively higher abundance than other PCB congeners in sediment cores. In contrast, lower chlorinated PCBs dominated in water samples across the same 7 lakes. Linear regression suggests higher log K_{OW} values will enhance the potential for partitioning to sediment relative to water.
- BDE-47:99 ratios showed TOC content dependence ($R=0.36$), likely due to the greater hydrophobicity of BDE-99 than BDE-47.
- γ-HBCD is the principal isomer, while β-HBCD consistently displayed the lowest contribution to ΣHBCDs. Linear regression suggests that increased relative abundance of γ-HBCD is consistent with fresh input of HBCD, in view of the fact that the commercial

product is predominantly γ-HBCD.

- The ratio of TBB:TBPH in surficial sediment samples across all sites (0.01-0.06, mean=0.02) is significantly lower than the ratio of approximately 3:1 (Ma et al., 2013) and 4:1 (Stapleton et al., 2008) in the commercial FM 550 flame retardant formulation, suggesting strongly that FM 550 is only a minor source of TBPH in the UK environment.

6.1.3 Suspended Sediment, Niagara River, Canada

- HBCDs in archived suspended sediment samples (n=39) collected over the period 1980-2012 at the mouth of the Niagara River in Lake Ontario showed temporal trends comparable with most of the English lakes, in which HBCD concentrations have declined or levelled-off from the early 2000s onwards.

- Suspended sediment samples taken in spring and summer of the period 2004-2012 revealed no statistical significant seasonal trends in HBCD concentrations, while English lake water samples showed higher average concentrations of ΣHBCDs in colder than warmer periods.

- The maximum ΣHBCD concentration in suspended sediments from the Niagara River is about 3 orders of magnitude lower than those detected in English lake water, which is plausible given the higher population density and use of HBCD in Europe than North America.

- While γ-HBCD dominated in all samples collected prior to 2002 inclusive (13-100%, mean=73%); the equivalent values were significantly lower (3.5-37%; mean=23%) for samples collected from 2003 onwards.

6.2 Research Gaps and Future Perspectives

The following issues are identified as warranting further investigation.

- Follow-up monitoring on sediments from English lakes is essential to further assess the temporal trends of target POPs and environmental response to changes in manufacture and use patterns of these POPs.

- Further and deeper investigation is required into the sources of POPs in English lakes. Particularly valuable would be the inclusion of additional potentially influencing factors such

as: the number and general processing capacity of sewage treatment plants within the catchment area of each lake, the existence of any industrial waste discharges into lakes, and the prevailing wind direction in relation to potential sources.

- To further elucidate the pathways of POPs from emission sources into lakes, parallel studies on surrounding environments should be conducted. Such environmental compartments should include outdoor air, soil, grass, and tree bark.

- Despite the historically and currently increasing use of certain NBFRs in the UK - reflected by the generally increasing temporal trends of these compounds in lake sediment cores in this study; there is a striking gap in our knowledge of the extent of NBFR contamination of lacustrine organisms. Such knowledge is an essential pre-requisite if their ecological effects in lacustrine systems are to be evaluated.

References

Abdallah, M., 2009. Investigating the sources and magnitude of human exposure to halogenated organic pollutants using advanced methods for environmental analysis. PhD thesis, University of Birmingham.

Abdallah, M.A., Harrad, S., 2009. Personal exposure to HBCDs and its degradation products via ingestion of indoor dust. Environ. Int. 35, 870-6.

Abdallah, M.A., Harrad, S., 2011. Tetrabromobisphenol-A, hexabromocyclododecane and its degradation products in UK human milk: relationship to external exposure. Environ. Int. 37, 443-8.

Abdallah, M.A., Harrad, S., 2014. Polybrominated diphenyl ethers in UK human milk: Implications for infant exposure and relationship to external exposure. Environ. Int. 63, 130-6.

Abdallah, M.A., Harrad, S., Covaci, A., 2008. Hexabromocyclododecanes and tetrabromobisphenol-A in indoor air and dust in Birmingham, U.K: implications for human exposure. Environ. Sci. Technol. 42, 6855-61.

Abdallah, M.A., Harrad, S., Covaci, A., 2009. Isotope Dilution Method for Determination of Polybrominated Diphenyl Ethers Using Liquid Chromatography Coupled to Negative Ionization Atmospheric Pressure Photoionization Tandem Mass Spectrometry: Validation and Application to House Dust. Anal. Chem. 81, 7460-7.

Abdallah, M.A., Morsy, F.A., 2013. Persistent organochlorine pollutants and metals residues in sediment and freshwater fish species cultured in a shallow lagoon, Egypt. Environ. Technol. 34, 2389-99.

Alaee, M., Arias, P., Sjodin, A., Bergman, A., 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environ. Int. 29, 683-9.

Ali, N., Dirtu, A.C., Van den Eede, N., Goosey, E., Harrad, S., Neels, H., 't Mannetje, A., Coakley, J., Douwes, J., Covaci, A., 2012. Occurrence of alternative flame retardants in indoor dust from New Zealand: indoor sources and human exposure assessment. Chemosphere. 88, 1276-82.

Ali, N., Harrad, S., Goosey, E., Neels, H., Covaci, A., 2011a. "Novel" brominated flame retardants in Belgian and UK indoor dust: implications for human exposure. Chemosphere 83, 1360-5.

Ali, N., Harrad, S., Muenhor, D., Neels, H., Covaci, A., 2011b. Analytical characteristics and determination of major novel brominated flame retardants (NBFRs) in indoor dust. Anal. Bioanal. Chem. 400, 3073-83.

Allchin, C.R., Law, R.J., Morris, S. 1999. Polybrominated diphenyl ethers in sediments and biota downstream of potential sources in the UK. Environ. Pollut. 105, 197-207.

Anderson, D.J., Bloem, T.B., Blankenbaker R.K., Stanko, T.A., 1999. Concentration of Polychlorinated Biphenyls in the water column of the Laurentian Great Lakes: spring 1993. J. Great Lakes Res. 25, 160-70.

Andersson, P.L., Öberg, K., Örn, U., 2006. Chemical characterization of brominated flame retardants and identification of structurally representative compounds. Environ. Toxicol. Chem. 25, 1275-82.

Appleby, P.G, 2001. Chronostratigraphic techniques in recent sediments. In: Last, W.M., and Smol, J.P. (eds.) Tracking Environmental Change Using Lake Sediments. Vol. 1: Basin Analysis, Coring, and Chronological Techniques. Kluwer Academic Publishers, Dordrecht, Netherland. 171-203.

Appleby, P.G., Nolan, P.J., Gifford, D.W., Godfrey, M.J., Oldfield, F., Anderson, N.J, Battarbee, R.W., 1986. 210Pb dating by low background gamma counting. Hydrobiologia, 141, 21-27.

Appleby, P.G., Richardson, N., Nolan, P.J., 1992. Self-absorption corrections for well-type germanium detectors. Nucl. Inst. & Methods B. 71, 228-233.

Arias, P.A., 2001. Brominated flame retardants-An overview. The Second International Workshop on Brominated Flame Retardants. Stockholm. 17-9.

Arp, H.P., Møskeland, T., Andersson, P.L., Nyholm, J.R., 2011. Presence and partitioning properties of the flame retardants pentabromotoluene, pentabromoethylbenzene and hexabromobenzene near suspected source zones in Norway. J. Environ. Monit. 13, 505-13.

Asante, K.A., Takahashi, S., Itai, T., Isobe, T., Devanathan, G., Muto, M., Agyakwah, S.K., Adu-Kumi, S., Subramanian, A., Tanabe, S., 2013. Occurrence of halogenated contaminants in inland and coastal fish from Ghana: levels, dietary exposure assessment and human health implications. Ecotoxicol. Environ. Saf. 94, 123-30.

ATSDR, 2000. Toxicological profile for the polychlorinated biphenyls (updated). Agency for toxic substances and disease registry, Atlanta, US.

Bamford, H.A., Ko, F.C., Baker, J.E., 2002. Seasonal and Annual Air-Water Exchange of Polychlorinated Biphenyls across Baltimore Harbor and the Northern Chesapeake Bay. Environ. Sci. Technol. 36, 4245-52.

Barakat, A.O., Khairy, M., Aukaily, I., 2013. Persistent organochlorine pesticide and PCB residues in surface sediments of Lake Qarun, a protected area of Egypt. Chemosphere 90, 2467-76.

Barón, E., Gago-Ferrero, P., Gorga, M., Rudolph, I., Mendoza, G., Zapata, A.M., Díaz-Cruz, S., Barra, R., Ocampo-Duque, W., Páez, M., Darbra, R.M., Eljarrat, E., Barceló, D., 2013. Occurrence of hydrophobic organic pollutants (BFRs and UV-filters) in sediments from

South America. Chemosphere 92, 309-16.

Becher, G., 2005. The stereochemistry of 1,2,5,6,9,10-hexabromocyclododecane and its graphic representation. Chemosphere 58, 989-991.

Benická, E., Takáčová, D., Krupčik, J., Skačáni, I., Onuska, F., Terry, K., 1998. Gas chromatographic separation of PCB atropisomers on cyclodextrin stationary phases. Chirality 10, 540-7.

Bhatt, P., Kumar, M.S., Mudliar, S., Chakrabarti, T., 2007. Biodegradation of chlorinated compounds-a review. Critical Reviews in Environ. Sci. Technol. 37, 165-98.

Bidleman, T.F., 1988. Atmospheric processes: wet and dry deposition of organic compounds are controlled by their vapour-particle partitioning. Environ. Sci. Technol. 22, 361-7.

Bignert, A., Olsson, M., Persson, W., Jensen, S., Zakrisson, S., Litzen, K., Eriksson, U., Haggberg, L., Alsberg, T., 1998. Temporal trends of organochlorines in Northern Europe, 1967-1995. Relation to global fractionation, leakage from sediments and international measures. Environ. Pollut. 99, 177-98.

Birgul, A., Katsoyiannis, A., Gioia, R., Crosse, J., Earnshaw, M., Ratola, N., Jones, K.C., Sweetman, A.J., 2012. Atmospheric polybrominated diphenyl ethers (PBDEs) in the United Kingdom. Environ. Pollut. 169, 105-11.

Bogdal, C., Scheringer, M., Schmid, P., Bläuenstein, M., Kohler, M., Hungerbühler, K., 2010. Levels, fluxes and time trends of persistent organic pollutants in Lake Thun, Switzerland: Combining trace analysis and multimedia modeling. Sci. Total Environ. 408, 3654-63.

Bogdal, C., Schmid, P., Kohler, M., Müller, C.E., Iozza, S., Bucheli, T.D., Scheringer, M., Hungerbühler, K., 2008. Sediment record and atmospheric deposition of brominated flame retardants and organochlorine compounds in Lake Thun, Switzerland: lessons from the past and evaluation of the present. Environ. Sci. Technol. 42, 6817-22.

Booij, K., Zegers, B.N., Boon, J.P., 2002. Levels of some polybrominated diphenyl ether (PBDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels (Mytilus edulis). Chemosphere 46, 683-8.

Borghesi, N., Corsolini, S., Leonards, P., Brandsma, S., De Boer, J., Focardi, S., 2009. Polybrominated diphenyl ether contamination levels in fish from the Antarctic and the Mediterranean Sea. Chemosphere, 77, 693-8.

Borja, J., Taleon, D.M., Auresenia, J., Gallardo, S., 2005. Polychlorinated biphenyls and their biodegradation. Process Biochemistry 40, 1999-2013.

Bouchard, M.F., Oulhote, Y., Sagiv, S.K., Saint-Amour, D., Weuve, J., 2014. Polychlorinated Biphenyl Exposures and Cognition in Older U.S. Adults: NHANES (1999-2002). Environ. Health. Perspect. 122, 73-8.

Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical emission

inventory for selected PCB congeners - a mass balance approach: 1. Global production and consumption. Sci. Total Environ. 290, 181-98.

Brorstrom-Lunden, E., 1996. Atmospheric deposition of persistent organic compounds to the sea surface. J. Sea Research 35, 81-90.

Bruhn, R., McLachlan, M.S., 2002. Seasonal variation of polychlorinated biphenyl concentrations in the southern part of the Baltic Sea. Mar. Pollut. Bull. 44, 156-63.

BSEF2006. Bromine Science and Environmental Forum, http://www.bsef.com/

BSEF2013. Bromine Science and Environmental Forum. http://www.bsef.com/index.php?mact=MediaRoom,cntnt01,details,0&cntnt01documentid=629&cntnt01dateformat=%25A%20%25d%20%25B%20%25Y&cntnt01returnid=162

Buckman, A.H., Wong, C.S., Chow, E.A., Brown, S.B., Solomon, K.R., Fisk, A.T., 2006. Biotransformation of polychlorinated biphenyls (PCBs) and bioformation of hydroxylated PCBs in fish. Aquat. Toxicol. 78, 176-85.

Budakowski, W., Tomy, G., 2003. Congener-specific analysis of hexabromocyclododecane by high-performance liquid chromatography/electrospray tandem mass spectrometry. Rapid Commun. Mass Spectrom. 17, 1399-404.

Cai, Y.Y., 2008. Current major brominated flame retardants. Handbook of Modern Technology of Flame Retardarce, 35-45 (in Chinese).

Cailleaud, K., Forget-Leray, J., Souissi, S., Hilde, D., LeMenach, K., Budzinski, H., 2007. Seasonal variations of hydrophobic organic contaminant concentrations in the water-column of the Seine Estuary and their transfer to a planktonic species Eurytemora affinis (Calanoïda, copepoda). Part 1: PCBs and PAHs. Chemosphere 70, 270-80.

Carignan, C.C., Abdallah, M.A., Wu, N., Heiger-Bernays, W., McClean, M.D., Harrad, S., Webster, T.F., 2012. Predictors of tetrabromobisphenol-A (TBBP-A) and hexabromocyclododecanes (HBCD) in milk from Boston mothers. Environ. Sci. Technol. 46, 12146-53.

Chemtura, Material Safety Data Sheet, 2006. MSDS Number: 00896. Product Name: Firemaster® 550.

Chen, M.Y., Yu, M., Luo, X.J., Chen, S.J., Mai, B.X., 2011. The factors controlling the partitioning of polybrominated diphenyl ethers and polychlorinated biphenyls in the water-column of the Pearl River Estuary in South China. Mar. Pollut. Bull. 62, 29-35.

Chen, S.J., Luo, X.J., Lin, Z., Luo, Y., Li, K.C., Peng, X.Z., Mai, B.X., Ran, Y., Zeng, E.Y., 2007. Time trends of polybrominated diphenyl ethers in sediment cores from the Pearl River Estuary, South China. Environ. Sci. Technol. 41, 5595-600.

Chen, S.J., Ma, Y.J., Wang, J., Chen, D., Luo, X.J., Mai, B.X., 2009. Brominated flame retardants in children's toys: concentration, composition, and children's exposure and risk assessment.

Environ. Sci. Technol. 43, 4200-6.

Covaci, A., de Boer, J., Ryan, J.J., Voorspoels, S., Schepens, P., 2002. Distribution of organobrominated and organochlorinated contaminants in Belgian human adipose tissue. Environ. Res. 88, 210-8.

Covaci, A., Gerecke, A.C., Law, R. J., Voorspoels, S., Kohler, M., Heeb, N. V., Leslie, H., Allchin, C. R., De Boer, J., 2006. Hexabromocyclododecanes (HBCDs) in the environment and humans: A review. Environ. Sci. Technol. 40, 3679-88.

Covaci, A., Harrad, S., Abdallah, M.A., Ali, N., Law, R.J., Herzke, D., de Wit, CA., 2011. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environ. Int. 37, 532-56.

Covaci, A., Roosens, L., Dirtu, A.C., Waegeneers, N., Van Overmeire, I., Neels, H., Goeyens, L., 2009. Brominated flame retardants in Belgian home-produced eggs: levels and contamination sources. Sci. Total Environ. 407, 4387-96.

Cristale, J., García Vázquez, A., Barata, C., Lacorte, S., 2013. Priority and emerging flame retardants in rivers: occurrence in water and sediment, Daphnia magna toxicity and risk assessment. Environ. Int. 59, 232-43.

da Silva, S.F., Brüning, I.M., Montone, R.C., Taniguchi, S., Cascaes, M.J., Dias, P.S., Lavandier, R.C., Hauser-Davis, R.A., Moreira, I., 2013. Polybrominated diphenyl ethers (PBDES) and polychlorinated biphenyls (PCBS) in mussels and two fish species from the estuary of the Guanabara Bay, Southeastern Brazil. Bull. Environ. Contam. Toxicol. 91, 261-6.

Darnerud, P.O., Atuma, S., Aune, M., Cnattingius, S., Wernroth, M.L., Wicklund, G.A., 1998. Polybrominated diphenyl ethers (PBDEs) in breast milk from primiparous women in Uppsala County, Sweden. Organohalog Compd. 35, 411-4.

Davis, J.W., Gonsior, S., Marty, G., Ariano, J., 2005. The transformation of hexabromocyclododecane in aerobic and anaerobic soils and aquatic sediments. Water Res. 39, 1075-84.

de la Cal, A., Eljarrat, E., Barcelo´ , D., 2003. Determination of 39 polybrominated diphenyl ether congeners in sediment samples using fast selective pressurized liquid extraction and purification. J. Chromatogr. A. 1021, 165-73.

de Wit, C.A., Herzke, D., Vorkamp, K., 2010. Brominated flame retardants in the Arctic environment-trends and new candidates. Sci. Total Environ. 408, 2885-918.

D'Hollander, W., Roosens, L., Covaci, A., Cornelis, C., Reynders, H., Campenhout, K.V., Voogt, Pd., Bervoets, L., 2010. Brominated flame retardants and perfluorinated compounds in indoor dust from homes and offices in Flanders, Belgium. Chemosphere 81, 478-87.

Dirtu, A.C., Ali, N., Van den Eede, N., Neels, H., Covaci, A., 2012. Country specific comparison for profile of chlorinated, brominated and phosphate organic contaminants in indoor dust.

Case study for Eastern Romania, 2010. Environ. Int. 49, 1-8.

Dodder, N.G., Strandberg, B., Hites, R.A., 2002. Concentrations and Spatial Variations of Polybrominated Diphenyl Ethers and Several Organochlorine Compounds in Fishes from the Northeastern United States. Environ. Sci. Technol. 2002, 36, 146-51.

Drage, D., 2013. Brominated micropollutants within the integrated steel-making process and their fate in the environment. PhD thesis.

Driffield, M., Harmer, N., Bradley, E., Fernandes, A.R., Rose, M., Mortimer, D., Dicks, P., 2008. Determination of brominated flame retardants in food by LC-MS/MS: diastereoisomer-specific hexabromocyclododecane and tetrabromobisphenol A. Food Addit. Contam. 25, 895-903.

Eisenreich, S.J., Capel, P.D., Robbins, J.A., Bourbonniere, R., 1989. Accumulation and diagenesis of cholorinated hydrocarbons in lacustrine sediments. Environ. Sci. Technol. 23, 1116-26.

Eljarrat, E., de la Cal, A., Raldua, D., Duran, C., Barceló, D., 2004. Occurrence and bioavailability of polybrominated diphenyl ethers and hexabromocyclododecane in sediment and fish from the Cinca River, a tributary of the Ebro River (Spain). Environ. Sci. Technol. 38, 2603-8.

EPA (Danish Environmental Protection Agency), 2007. Deca-BDE and alternatives in electrical and electronic equipment. http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/html/kap05_eng.htm.

Eriksson, P., Fischer, C., Wallin, M., Jakobsson, E., Fredriksson, A., 2006. Impaired behaviour, learning and memory, in adult mice neonatally exposed to hexabromocyclododecane (HBCDD). Environ. Toxicol. Pharmacol. 21, 317-22.

ESIS. European Chemical Substance Information System. European Commission, Joint Research Centre, European Chemicals Bureau; 2010.

Esposito, M., Serpe, F.P., Diletti, G., Messina, G., Scortichini, G., La Rocca, C., Baldi, L., Amorena, M., Monda, M., 2014. Serum levels of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls in a population living in the Naples area, southern Italy. Chemosphere. 94, 62-9.

Esslinger, S., Becker, R., Jung, C., Schröter-Kermani, C., Bremser, W., Nehls, I., 2011. Temporal trend (1988-2008) of hexabromocyclododecane enantiomers in herring gull eggs from the German coastal region. Chemosphere 83,161-7

EU RISK ASSESSMENT REPORT 2002. European Union Risk Assessment Report on Bis(pentabromophenyl) ether. European Commission, Joint Research Centre, European Chemicals Bureau, EUR20402EN, 2002, Vol. 17.

European Commission. http://ec.europa.eu/environment/pops/index_en.htm

European Court of Justice, 2008. Joined Cases C-14/06 and C-295/06, Judgement of the Court, 1 April 2008, Directive 2002/95/EC and Commission Decision 2005/717/EC..

Fängström, B., Athanassiadis, I., Odsjö, T., Norén, K., Bergman,A., 2008. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in milk from Stockholm mothers, 1980-2004. Mol. Nutr. Food Res. 52, 187-93.

Fernandes, A., Smith, F., Petch, R., Panton, S., Carr, M., Mortimer, D., Tlustos, C., Rose, M., 2010. The emerging BFRs Hexabromobenzene (HBB), Bis-(2,4,6-tribromophenoxy)ethane (BTBPE), and Decabromodiphenylethane (DBDPE) in UK and Irish Foods. Proceedings BFR 2010, Kyoto, Japan. 90028.

Field, J.A., Sierra-Alvarez, R., 2008. Microbial transformation and degradation of polychlorinated biphenyls. Environ. Pollut. 155, 1-12.

Fitzgerald, E.F., Belanger, E.E., Gomez, M.I., Cayo, M., McCaffrey, R.J., Seegal, R.F., Jansing, R.L., Hwang, S.A., Hicks, H.E., 2008. Polychlorinated biphenyl exposure and neuropsychological status among older residents of upper Hudson River communities. Environ. Health. Perspect. 116, 209-15.

Fowles, J.R., Fairbrother, A., Baechersteppan, L., Kerkvliet, N.I., 1994. Immunological and endocrine effects of the flame-retardant pentabromodiphenyl ether (DE-71) in C57Bl/6J mice. Toxicology. 86, 49-61.

Frederiksen, M., Vorkamp, K., Thomsen, M., Knudsen, L.E., 2009. Human internal and external exposure to PBDEs-a review of levels and sources. Int. J of Hyg. Environ. Health. 212, 109-34.

Fu. J., Wang, Y., Zhang, A., Zhang, Q., Zhao, Z., Wang, T., Jiang, G., 2011. Spatial distribution of polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs) in an e-waste dismantling region in Southeast China: Use of apple snail (Ampullariidae) as a bioindicator. Chemosphere 82, 648-55.

Fujii, Y., Harada, K.H., Hitomi, T., Kobayashi, H., Koizumi, A., Haraguchi, K., 2014. Temporal trend and age-dependent serum concentration of phenolic organohalogen contaminants in Japanese men during 1989-2010. Environ. Pollut. 185, 228-33.

Gauthier, L.T., Hebert, C.E., Weseloh, D.V.C., Letcher, R.J., 2007. Current-use flame retardants in the eggs of herring gulls (Larus argentatus) from the Laurentian Great Lakes. Environ. Sci. Technol. 41, 4561-7.

Gerecke, A.C., Giger, W., Hartmann, P.C., Heeb, N.V., Kohler, H.-P.E., Schmid, P., Zennegg, M., Kohler, M., 2006. Anaerobic degradation of brominated flame retardants in sewage sludge. Chemosphere 64, 311-7.

Germer, S., Piersma, A.H., van der Ven, L., Kamyschnikow, A., Fery, Y., Schmitz, H.J., Schrenk, D. 2006. Subacute effects of the brominated flame retardants hexabromocyclododecane and

tetrabromobisphenol-A on hepatic cytochrome P450 levels in rats. Toxicology 218, 229-36.

Gevao, B., Hamilton-Taylor, J., Jones, K.C., 1998. Polychlorinated biphenyl and polycyclic aromatic hydrocarbon deposition to and exchange at the air-water interface of Esthwaite Water, a small lake in Cumbria, UK. Environ. Pollut. 102, 63-75.

Gevao, B., John Hamilton-Taylor, J., Murdoch, C., Jones, K.C., Kelly, M., Tabner, B.J., 1997. Depositional time trends and remobilization of PCBs in Lake sediments. Environ. Sci. Technol. 31, 3274-80.

Gomara, B., Herrero, L., Ramos, J.J., Mateo, J.R., Fernandez, M.A., Garcia, J.F., Gonzalez, M.J. 2007. Distribution of polybrominated diphenyl ethers inhumanumbilical cord serum, paternal serum, maternal serum, placentas, and breast milk from Madrid population, Spain. Environ. Sci. Technol. 41, 6961-8.

Gorga, M., Martínez, E., Ginebreda, A., Eljarrat, E., Barceló, D., 2013. Determination of PBDEs, HBB, PBEB, DBDPE, HBCD, TBBPA and related compounds in sewage sludge from Catalonia (Spain). Sci. Total Environ. 444, 51-9.

Gouin, T., Harner, T., Blanchard, P., Mackay, D., 2005. Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes Basin. Environ. Sci. Technol. 39, 9115-22.

Goutte, A., Chevreuil, M., Alliot, F., Chastel, O., Cherel, Y., Eléaume, M., Massé, G., 2013. Persistent organic pollutants in benthic and pelagic organisms off Adélie Land, Antarctica. Mar. Pollut. Bull. 77, 82-9.

Guan Y.F., Wang J.Z., Ni, H.G., Zeng, E.Y., 2009. Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: Assessment of mass loading, input source and environmental fate. Environ. Pollut. 157, 618-24.

Guerra, P., de la Cal, A., Marsh, G., Eljarrat, E., Barcelo, D., 2009. Transfer of hexabromocyclododecane from industrial effluents to sediments and biota: Case study in Cinca river (Spain). J. Hydrol. 369, 360-367.

Guerra, P., Eljarrat, E., Barceló, D., 2010. Analysis and occurrence of emerging brominated flame retardants in the Llobregat River basin. J. Hydrol. 383, 39-43.

Guzzella, L., Roscioli, C., Binelli, A., 2008. Contamination by polybrominated diphenyl ethers of sediments from the Lake Maggiore basin (Italy and Switzerland). Chemosphere 73, 1684-91.

Haase, R.F., McCaffrey, R.J., Santiago-Rivera, A.L., Morse, G.S., Tarbell, A., 2009. Evidence of an age-related threshold effect of polychlorinated biphenyls (PCBs) on neuropsychological functioning in a Native American population. Environ. Res. 109, 73-85

Hale, R.C., La Guardia, M.J., Harvey, E., Gaylor, M.O., Mainor, T.M., 2006. Brominated flame retardant concentrations and trends in abiotic media. Chemosphere 64, 181-6.

Harju, M., Heimstad, E.S., Herzke, D., Sandanger, T., Posner, S., Wania, F., Emerging "new" brominated flame retardants in flame retarded products and the environment. Report 2462. Oslo, Norway: Norwegian Pollution Control Authority; 2009. 113.

Harrad, S., Abdallah, M.A., Rose, N.L., Turner, S.D., Davidson, T.A., 2009. Current-use brominated flame retardants in water, sediment, and fish from English lakes. Environ. Sci. Technol. 43, 9077-83.

Harrad, S., Goosey, E., Desborough, J., Abdallah, M.A.E., Roosens, L., Covaci, A., 2010. Dust from UK primary school classrooms and daycare centers: the significance of dust as a pathway of exposure of young UK children to brominated flame retardants and polychlorinated biphenyls. Environ. Sci. Technol. 44, 4198-202.

Harrad, S., Hazrati, S., Ibarra, C., 2006. Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: implications for human exposure. Environ. Sci. Technol. 40, 4633-8.

Harrad, S., Hunter, S., 2006. Concentrations of polybrominated diphenyl ethers in air and soil on a rural-urban transect across a major UK conurbation. Environ. Sci. Technol. 40, 4548-53.

Harrad, S., Ibarra, C., Abdallah, M.A., Boon, R., Neels, H., Covaci, A., 2008a. Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and offices: causes of variability and implications for human exposure. Environ. Int. 34, 1170-5.

Harrad, S., Ibarra, C., Diamond, M.L., Melymuk, L., Robson, M., Douwes, J., Roosens, L., Dirtu, A.C., Covaci, A., 2008b. Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States. Environ. Int. 34, 232-38.

Harrad, S., Porter, L., 2007. Concentrations of polybrominated diphenyl ethers in blood serum from New Zealand. Chemosphere 66, 2019-23.

Harrad, S., Wijesekera, R., Hunter, S., Halliwell, C., Baker, R., 2004. A preliminary assessment of UK human dietary and inhalation exposure to polybrominated diphenyl ethers. Environ. Sci. Technol. 38, 2345-50.

Harrad, S.J., Sewart, A.P., Alcock, R., Boumphrey, R., Burnett, V., Duarte-Davidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S.R., Jones, K.C., 1994. Polychlorinated biphenyls (PCBs) in the British environment: sinks, sources and temporal trends. Environ. Pollut. 85, 131-46.

HBCD Factsheet, BSEF, 2012. http://www.bsef.com/uploads/Factsheet_HBCD_25-10-2012.pdf

He, M.J., Luo, X.J., Yu, L.H., Wu, J.P., Chen, S.J., Mai, B.X., 2013. Diasteroisomer and enantiomer-specific profiles of hexabromocyclododecane and tetrabromobisphenol A in an aquatic environment in a highly industrialized area, South China: vertical profile, phase partition, and bioaccumulation. Environ. Pollut. 179,105-10.

Health Effects of PCBs. U.S. Environmental Protection Agency. January 31, 2013.

Heeb, N.V., Schweizer, W.B., Kohler, M., Gerecke, A.C., 2005. Structure elucidation of hexabromocyclododecanessa class of compounds with a complex stereochemistry. Chemosphere 61, 65-73.

Hess, G. Industry drops flame retardant. Chem. Eng. News 2010, 88, 10.

Hites, R.A., 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environ. Sci. Technol. 38, 945-56.

Hoh, E., Hites, R. A., 2005. Brominated flame retardants in the atmosphere of the east-central United States. Environ. Sci. Technol. 39, 7794-7802.

Hoh, E., Zhu, L., Hites, R.A., 2005. Novel flame retardants, 1, 2-Bis(2, 4, 6-tribromophenoxy)ethane and 2, 3, 4, 5, 6-pentabromoethylbenzene, in United States' environmental samples. Environ. Sci. Technol. 39, 2472-7.

Hu, G.C., Luo, X.J., Dai, J.Y., Zhang, X.L., Wu, H., Zhang, C.L., Guo, W., Xu, M.Q., Mai, B.X., We, F.W., 2008. Brominated flame retardants, polychlorinated biphenyls, and organochlorine pesticides in giant panda (Ailuropoda melanoleuca) and red panda (Ailurus fulgens) from China. Environ. Sci. Technol. 42, 4704-9.

Ikonomou, M.G., Kelly, B.C., Stern, G.A., 2005. Spatial and temporal trends of PBDEs in biota from the Canadian Arctic marine environment. Organohalog Compd. 67, 950-3.

Ikonomou, M.G., Rayne, S., Addison, R.F., 2002. Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian arctic from 1981 to 2000. Environ. Sci. Technol. 36, 1886-92.

Inoue, K., Harada, K., Takenaka, K., Uehara, S., Kono, M., Shimizu, T., Takasuga, T., Senthilkumar, K., Yamashita, F., Koizumi, A., 2006. Levels and concentration ratios of polychlorinated biphenyls and polybrominated diphenyl ethers in serum and breast milk in Japanese mothers. Environ. Health. Perspect. 114, 1179-85.

Iwata, H., Tanabe, S., Sakai, N., Nishimura, A., Tatsukawa, R., 1994. Geographical distribution of organochlorines in air, water and sediments from Asia and Oceania and their implications for global redistribution from lower latitudes. Environ. Pollut. 85, 15-33.

Jamshidi, A., Hunter, S., Hazrati, S., Harrad, S., 2007. Concentrations and chiral signatures of polychlorinated biphenyls in outdoor and indoor air and soil in a major UK conurbation. Environ. Sci. Technol. 41, 2153-8.

Jiao, L., Zheng, G.J., Minh, T.B., Richardson, B., Chen, L., Zhang, Y., Yeung, L.W., Lam, J.C., Yang, X., Lam, P.K., Wong, M.H., 2009. Persistent toxic substances in remote lake and coastal sediments from Svalbard, Norwegian Arctic: levels, sources and fluxes. Environ. Pollut. 157, 1342-51.

Jin, J., Wang, Y., Yang, C., Hu, J., Liu, W., Cui, J., Tang, X., 2009. Polybrominated diphenyl ethers in the serum and breast milk of the resident population from production area, China.

Environ. Int. 35, 1048-52.

Johnson, P.I., Stapleton, H.M., Mukherjee, B., Hauser, R., Meeker, J.D., 2013. Associations between brominated flame retardants in house dust and hormone levels in men. Sci. Total Environ. 445-6, 177-84.

Johnson-Restrepo, B., Adams, D.H., Kannan, K., 2008. Tetrabromobisphenol A (TBBPA) and hexabromocyclododecanes (HBCDs) in tissues of humans, dolphins, and sharks from the United States. Chemosphere. 70, 1935-44.

Johnson-Restrepo, B., Kannan, K., Addink, R., Adams, D.H., 2005a. Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. Environ. Sci. Technol. 39, 8243-50.

Johnson-Restrepo, B., Kannan, K., Rapaport, D.P., Rodan, B.D., 2005b. Polybrominated diphenyl ethers and polychlorinated biphenyls in human adipose tissue from New York. Environ. Sci. Technol. 39, 5177-82.

Jones-Otazo, H.A., Clarke, J.P., Diamond, M.L., Archbold, J.A., Ferguson, G., Harner, T., Richardson, G.M., Ryan, J.J., Wilford, B., 2005. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. Environ. Sci. Technol. 39, 5121-30.

Julander, A., Karlsson, M., Hagstrom, K., Ohlson, C.G., Engwall, M., Bryngelsson, I.L., Westberg, H., van Bavel, B. 2005. Polybrominated diphenyl ethers-plasma levels and thyroid status of workers at an electronic recycling facility. Int. Arch. Occup. Environ. Health. 78, 584-92.

Jürgens, M.D., Johnson, A.C., Jones, K.C., Hughes, D., Lawlor, A.J., 2013. The presence of EU priority substances mercury, hexachlorobenzene, hexachlorobutadiene and PBDEs in wild fish from four English rivers. Sci. Total Environ. 461-2, 441-52.

Karlsson, M., Julander, A., van Bavel, B., Hardell, L., 2007. Levels of brominated flame retardants in blood in relation to levels in household air and dust. Environ. Int. 33, 62-9.

Keller, J.M., Stapleton, H.M., Heltsley, R., Peck, A., Kucklick, J.R., Schantz, M., Wise, S.A., 2007. SRMs available from NIST for the analysis of brominated flame retardants. Poster presented at BFR2007, Amsterdam, The Netherlands.

KEMI (National Chemicals Inspectorate) 2007. Final draft of the EU Risk Assessment Report on Hexabromocyclododecane R044_0710_env_hh.doc. R044_0710_env_hh.doc; Sundbyberg, Sweden

Kemp, A.L.W., Harper, N.S., 1976. Sedimentation rates and a sedimentation budget for Lake Ontario. J. Great Lakes Res. 2, 324-40.

Kierkegaard, A., Bjorklund, J., Friden, U., 2004. Identification of the flame retardant decabromodiphenyl ethane in the environment. Environ. Sci. Technol. 38, 3247-53.

Kilemade, M., Hartl, M.G.J., Sheehan, D., Mothersill, C., van Pelt, F.N.A.M., O'Brien, N.M., O'Halloran, J., 2004. An assessment of the pollutant status of surficial sediment in Cork Harbour in the South East of Ireland with particular reference to polycyclic aromatic hydrocarbons. Mar. Pollut. Bull. 49, 1084-96.

Klosterhaus, S.L., Stapleton, H.M., La Guardia, M.J., Greig, D.J., 2012. Brominated and chlorinated flame retardants in San Francisco Bay sediments and wildlife. Environ. Int. 47, 56-65.

Kohler, M., Zennegg, M., Bogdal, C., Gerecke, A.C., Schmid, P., Heeb, N.V., Sturm, M., Vonmont, H., Kohler, H.E., Giger, W., 2008. Temporal trends, congener patterns, and sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and hexabromocyclododecanes (HBCD) in Swiss lake sediments. Environ. Sci. Technol. 42, 6378-84.

La Guardia, M.J., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ. Sci. Technol. 40, 6247-54.

La Guardia, M.J., Hale, R.C., Newman, B., 2013. Brominated flame-retardants in Sub-Saharan Africa: burdens in inland and coastal sediments in the eThekwini metropolitan municipality, South Africa. Environ. Sci. Technol. 47, 9643-50.

Lailson-Brito, J., Dorneles, P.R., Azevedo-Silva, C.E., Bisi, T.L., Vidal, L.G., Legat, L.N., Azevedo, A.F., Torres, J.P., Malm, O., 2012. Organochlorine compound accumulation in delphinids from Rio de Janeiro State, southeastern Brazilian coast. Sci. Total Environ. 433, 123-31.

Lam, J.C.W., Lau, R.K.F., Murphy, M.B., Lam, P.K.S., 2009. Temporal trends of hexabromocyclododecanes (HBCDs) and polybrominated diphenyl ethers (PBDEs) and detection of two novel flame retardants in marine mammals from Hong Kong, south China. Environ. Sci. Technol. 43, 6944-9.

Lankova, D., Lacina, O., Pulkrabova, J., Hajslova, J., 2013. The determination of perfluoroalkyl substances, brominated flame retardants and their metabolites in human breast milk and infant formula. Talanta. 117, 318-25.

Law, K., Halldorson, T., Danell, R., Stern, G., Gewurtz, S., Alaee, M., Marvin, C., Whittle, M., Tomy, G., 2006. Bioaccumulation and trophic transfer of some brominated flame retardants in a Lake Winnipeg (Canada) food web. Environ. Toxicol. Chem. 25, 2177-86.

Law, R.J., Barry, J., Barber, J.L., Bersuder, P., Deaville, R., Reid, R.J., Brownlow, A., Penrose, R., Barnett, J., Loveridge, J., Smith, B., Jepson, P.D., 2012. Contaminants in cetaceans from UK waters: status as assessed within the Cetacean Strandings Investigation Programme from 1990 to 2008. Mar. Pollut. Bull. 64, 1485-94.

Law, R.J., Barry, J., Bersuder, P., Barber, J.L., Deaville, R., Reid, R.J., Jepson, P.D., 2010. Levels and trends of brominated diphenyl ethers in blubber of harbor porpoises (Phocoena phocoena) from the U.K., 1992-2008. Environ. Sci. Technol. 44, 4447-51.

Law, R.J., Losada, S., Barber, J.L., Bersuder, P., Deaville, R., Brownlow, A., Penrose, R., Jepson, P.D., 2013. Alternative flame retardants, Dechlorane Plus and BDEs in the blubber of harbour porpoises (Phocoena phocoena) stranded or bycaught in the UK during 2008. Environ. Int. 60, 81-8.

Li, H., Shang, H., Wang, P., Wang, Y., Zhang, H., Zhang, Q., Jiang, G., 2013. Occurrence and distribution of hexabromocyclododecane in sediments from seven major river drainage basins in China. J. Environ. Sci. (China). 25, 69-76.

Li, N., Wania, F., Lei, Y. D., and Daly. G.L., 2003. A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. J. Phys. Chem. Ref. Data. 32, 1545-90.

Litskas, V.D., Dosis, I.G., Karamanlis, X.N., Kamarianos, A.P., 2012. Occurrence of priority organic pollutants in Strymon river catchment, Greece: inland, transitional, and coastal waters. Environ. Sci. Pollut. Res. 19, 3556-67.

López, P., Brandsma, S.A., Leonards, P.E.G., de Boer, J., 2011. Optimization and development of analytical methods for the determination of new brominated flame retardants and polybrominated diphenyl ethers in sediments and suspended particulate matter. Anal. Bioanal. Chem. 400, 871-83.

Luo, X.J., Chen, S.J., Mai, B.X., Fu, J.M., Sci. 2010. Advances in the study of current-use non-PBDE brominated flame retardants and dechlorane plus in the environment and humans. Science China Chemistry. 53, 961-73.

Luo, X.J., Yu, M., Mai, B.X., Chen, S.J., 2008. Distribution and partition of polybrominated diphenyl ethers (PBDEs) in water of the Zhujiang River Estuary. Chinese Science Bulletin 53, 493-500.

Lyche, J.L., Grześ, I.M., Karlsson, C., Nourizadeh-Lillabadi, R., Berg, V., Kristoffersen, A.B., Skåre, J.U., Alestrøm, P., Ropstad, E., 2013. Parental exposure to natural mixtures of POPs reduced embryo production and altered gene transcription in zebrafish embryos. Aquat. Toxicol. 126, 424-34.

Ma, Y., Salamova, A., Venier, M., Hites, R.A., 2013. Has the phase-out of PBDEs affected their atmospheric levels? Trends of PBDEs and their replacements in the Great Lakes atmosphere. Environ. Sci. Technol. 47, 11457-64.

Mai, B., Chen, S., Luo, X., Chen, L., Yang, Q., Sheng, G., Peng, P., Fu J., Zeng, E.Y., 2005. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. Environ. Sci. Technol. 39, 3521-7.

Malarvannan, G., Isobe, T., Covaci, A., Prudente, M., Tanabe, S., 2013. Accumulation of brominated flame retardants and polychlorinated biphenyls in human breast milk and scalp hair from the Philippines: levels, distribution and profiles. Sci. Total Environ. 442, 366-79.

Mamontova, E.A., Mamontov, A.A., Tarasova, E.N., Kuzmin, M.I., Ganchimeg, D., Khomutova, M.Y., Gombosuren, O., Ganjuurjav, E., 2013. Polychlorinated biphenyls in surface soil in urban and background areas of Mongolia. Environ. Pollut. 182, 424-9.

Managaki, S., Enomoto, I., Masunaga, S., 2012. Sources and distribution of hexabromocyclododecanes (HBCDs) in Japanese river sediment. J. Environ. Monit. 14, 901-7.

Martin, M., Lam, P.K., Richardson, B.J., 2004. An Asian quandary: Where have all of the PBDEs gone? Mar. Pollut. Bull. 49, 375-82.

Marvin, C., Williams, D., Kuntz, K., Klawunn, P., Backus, S., Kolic, T., Lucaciu, C., MacPherson, K., Reiner, E., 2007. Temporal trends in polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like PCBs, and polybrominated diphenyl ethers in Niagara river suspended sediments. Chemophere 67, 1808-15.

Marvin, C.H., Tomy, G.T., Armitage, J.M., Arnot, J.A., McCarty, L., Covaci, A., Palace, V., 2011. Hexabromocyclododecane: Current Understanding of Chemistry, Environmental Fate and Toxicology and Implications for Global Management. Environ. Sci. Technol. 45, 8613-23.

McDonald, T.A., 2002. A perspective on the potential health risks of PBDEs. Chemosphere 46, 745-55.

McVeety, B.D., Hites, R.A., 1988. Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. Atmos. Environ. 22, 511-36.

Meironyté, D.; Norén, K.; Bergman, A., 1999. Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972-1997. J. Toxicol. Environ. Health. 58 Part A 329-41.

Meyer, T., Muir, D.C.G., Teixeira, C., Wang, X., Young, T., Wania, F., 2012. Deposition of Brominated Flame Retardants to the Devon Ice Cap, Nunavut, Canada. Environ. Sci. Technol. 46, 826-33.

Minh, N.H., Isobe, T., Ueno, D., Matsumoto, K., Mine, M., Kajiwara, N., Takahashi, S., Tanabe, S., 2007. Spatial distribution and vertical profile of polybrominated diphenyl ethers and hexabromocyclododecanes in sediment core from Tokyo Bay, Japan. Environ. Pollut. 148, 409-17.

Moret, I., Gambaro, A., Piazza, R., Ferrari, S., Manodori, L., 2005. Determination of polychlorobiphenyl congeners (PCBs) in the surface water of the Venice lagoon. Mar. Pollut. Bull. 50, 167-74.

Morris, S., Allchin, C.R., Zegers, B.N., Haftka, J.J., Boon, J.P., Belpaire, C., Leonards, P.E., van

Leeuwen, S.P., de Boer, J., 2004. Distribution and fate of HBCD and TBBPA brominated flame retardants in North Sea estuaries and aquatic food webs. Environ. Sci. Technol. 38, 5497-504.

Muenhor, D., Harrad, S., Ali, N., Covaci, A., 2010. Brominated flame retardants (BFRs) in air and dust from electronic waste storage facilities in Thailand. Environ. Int. 36, 690-8.

Muir, D.C.G., de Wit, C.A., 2010. Trends of legacy and new persistent organic pollutants in the circumpolar arctic: Overview, conclusions and recommendations. Sci. Total Environ. 408, 3044-51.

Muir, D.C.G., Omelchenko, A., Grift, N.P., Savoie, D.A., Lockhart, W.L., Wilkinson, P., Brunskill, G.J., 1996. Spatial trends and historical deposition of polychlorinated biphenyls in Canadian midlatitude and Arctic Lake sediments. Environ. Sci. Technol. 30, 3609-17.

Munschy, C., Héas-Moisan, K., Tixier, C., Boulesteix, L., Morin, J., 2011. Classic and novel brominated flame retardants (BFRs) in common sole (Solea solea L.) from main nursery zones along the French coasts. Sci. Total Environ. 409, 4618-27.

Nakata, H., Kawazoe, M., Arizono, K., Abe, S., Kitano, T., Shimada, H., 2002. Organochlorine pesticides and polychlorinated biphenyl residues in foodstuffs and human tissues from China: status of contamination, historical trend, and human dietary exposure. Arch. Environ. Contam. Toxicol. 43, 473-80.

Ni, H.G., Zeng, H., 2013. HBCD and TBBPA in particulate phase of indoor air in Shenzhen, China. Sci. Total Environ. 458-60,15-9.

Ni, H.G., Zeng, H., Tao, S., Zeng, E.Y., 2010. Environmental and human exposure to persistent halogenated compounds derived from e-waste in China. Environ. Toxicol. Chem. 29, 1237-47.

Niagara River Area of Concern, Canadian Section. Status of Beneficial use impairments, September 2010.

Nieminen, P., Lehtiniemi, H., Huusko, A., Vähäkangas, K., Rautio, A., 2013. Polychlorinated biphenyls (PCBs) in relation to secondary sex ratio-a systematic review of published studies. Chemosphere 91, 131-8.

Nomeir, A.A., Markham, P.M., Ghanayem, B.I., Chadwick, M., 1993. Disposition of the flame retardant 1,2(bis2,4,6-tribromophenoxy)ethane in rats following administration in the diet. Drug. Metab. Dispos. 21, 209-14.

Noren, K., Meironyte, D., 2000. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20-30 years. Chemosphere 40, 1111-23.

Nyholm, J.R., Grabic, R., Arp, H.P., Moskeland, T., Andersson, P.L., 2013. Environmental occurrence of emerging and legacy brominated flame retardants near suspected sources in Norway. Sci. Total Environ. 443, 307-14.

Nyholm, J.R., Lundberg, C., Andersson, P.L., 2010. Biodegradation kinetics of selected brominated flame retardants in aerobic and anaerobic soil. Environ. Pollut. 158, 2235-40.

Ondarza, P.M., Gonzalez, M., Fillmann, G., Miglioranza, K.S., 2014. PBDEs, PCBs and organochlorine pesticides distribution in edible fish from Negro River basin, Argentinean Patagonia. Chemosphere 94, 135-42.

Oram, J.J., McKee, L.J., Werme, C.E., Connor, M.S., Oros, D.R., Grace, R., Rodigari, F., 2008. A mass budget of polybrominated diphenyl ethers in San Francisco Bay, CA. Environ. Int. 34, 1137-47.

Oros, D.R., Hoover, D., Rodigari, F., Crane, D., Sericano, J., 2005. Levels and distribution of polybrominated diphenyl ethers in water, surface sediments, and bivalves from the San Francisco Estuary. Environ. Sci. Technol. 39, 33-41.

OSPAR list of substances of possible concern. Available at www.ospar.org.

Ou, X.Y., Li, J.J., 2006. An overview of brominated flame retardants. Flame Retardants: Quality, Manufacture and Application. 8-40 (in Chinese).

Palm, A., Cousins, I.T., Mackay, D., Tysklind, M., Metcalfe, C., Alaee, M., 2002. Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers. Environ. Pollut.117, 195-213.

Pan, X., Tang, J., Li, J., Zhong, G., Chen, Y., Zhang, G., 2011. Polybrominated diphenyl ethers (PBDEs) in the riverine and marine sediments of the Laizhou Bay area, North China. J. Environ. Monit., 2011, 13, 886-893.

Papachlimitzou, A., Barber, J.L., Losada, S., Bersuder, P., Law, R.J., 2012. A review of the analysis of novel brominated flame retardants. J. Chromatogr. A. 1219, 15-28.

Peled, M., Scharia, R., Sondack, D., 1995. Thermal rearrangement of hexabromo-cyclododecane (HBCD). Industrial Chemistry Library, Advances in Organobromine Chemistry II 7, 92-9.

Pettersson-Julander, A., van Bavel, B., Engwall, M., Westberg, H., 2004. Personal air sampling and analysis of polybrominated diphenyl ethers and other bromine containing compounds at an electronic recycling facility in Sweden. J. Environ. Monit. 6, 874-80.

Porta, M., Zumeta, E., 2002. Implementing the Stockholm Treaty on Persistent Organic Pollutants. Occup. Environ. Med 10, 651-2.

Qiu, X., Marvin, C.H., Hites, R.A., 2007. Dechlorane plus and other flame retardants in a sediment core from Lake Ontario. Environ. Sci. Technol. 41, 6014-9.

Qu, W., Bi, X., Sheng, G., Lu, S., Fu, J., Yuan, J., Li, L., 2007. Exposure to polybrominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. Environ. Int. 33, 1029-34.

Rapaport, R.A., Eisenreich, S.J., 1988. Historical atmospheric input of high molecular weight chlorinated hydrocarbons to Eastern North America. Environ. Sci. Technol. 22, 931-41.

Rawn, D.F., Gaertner, D.W., Weber, D., Curran, I.H., Cooke, G.M., Goodyer, C.G., 2014. Hexabromocyclododecane concentrations in Canadian human fetal liver and placental tissues. Sci. Total Environ. 468-9, 622-9.

Remberger, M., Sternbeck, J., Palm, A., Kaj, L., Strömberg, K., Brorström-Lundén, E., 2004. The environmental occurrence of hexabromocyclododecane in Sweden. Chemosphere 54, 9-21.

Rhind, S.M., Kyle, C.E., Kerr, C., Osprey, M., Zhang, Z.L., Duff, E.I., Lilly, A., Nolan, A., Hudson, G., Towers, W., Bell, J., Coull, M., McKenzie, C., 2013. Concentrations and geographic distribution of selected organic pollutants in Scottish surface soils. Environ. Pollut. 182:15-27.

Ricklund, N., Kierkegaard, A., McLachlan, M.S., 2010. Levels and potential sources of decabromodiphenyl ethane (DBDPE) and decabromodiphenyl ether (DecaBDE) in lake and marine sediments in Sweden. Environ. Sci. Technol. 44, 1987-91.

Robinet, T., Feunten, E., 2002. Sublethal effects of exposure to chemical compounds: a cause for the decline in Atlantic eels? Ecotoxicology 11, 265-277.

Roosens, L., Abdallah, M.A., Harrad, S., Neels, H., Covaci, A., 2009. Exposure to hexabromocyclododecanes (HBCDs) via dust ingestion, but not diet, correlates with concentrations in human serum: preliminary results. Environ. Health. Perspect. 117, 1707-12.

Rose, N.L., Rippey, B., 2002. The historical record of PAH, PCB, trace metal and fly-ash particle deposition at a remote lake in north-west Scotland. Environ. Pollut. 117,121-32.

Sacks, V.P., Lohmann, R., 2012. Freely dissolved PBDEs in water and porewater of an urban estuary. Environ. Pollut. 162, 287-93.

Salihoglu, G., Tasdemir, Y., Salihoglu, N.K., Baskaya, H.S., Aksoy, E., 2013. Seasonal variations of polychlorinated biphenyls in surface soils and air-soil exchange in Bursa, Turkey. Arch. Environ. Contam. Toxicol. 65, 619-34.

Sanders, G., Eisenreich, S.J., Jones, K.C., 1994. The rise and fall of PCBs: time-trend data from temperate industrialized countries. Chemosphere 29, 2201-8.

Sanders, G., Jones, K.C., Hamllton-Taylor, J., 1992. Historical inputs of polychlorinated biphenyls and other organochlorines to a dated lacustrine sediment core in rural England. Environ. Sci. Technol. 26, 1815-21.

Sawal, G., Stachel, B., Lepom, P., 2004. Polybrominated diphenyl ethers in sediments from the River Elbe, Germany. In: Proceedings of the Third International Workshop on Brominated Flame Retardants BFR2004, Toronto, Canada, 151-4.

Schantz, S.L., Gasior, D.M., Polverejan, E., McCaffrey, R.J., Sweeney, A.M., Humphrey, H.E., Gardiner, J.C., 2001. Impairments of memory and learning in older adults exposed to polychlorinated biphenyls via consumption of Great Lakes fish. Environ. Health. Perspect. 109, 605-11.

Schecter, A., Päpke, O., Tung, K.C., Joseph, J., Harris, T.R., Dahlgren, J., 2005. Polybrominated diphenyl ether flame retardants in the U.S. population: current levels, temporal trends, and comparison with dioxins, dibenzofurans, and polychlorinated biphenyls. J. Occup. Environ. Med. 47, 199-211.

Schuster, J.K., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M., Jones, K.C., 2010. Trends in European background air reflect reductions in primary emissions of PCBs and PBDEs. Environ. Sci. Technol. 44, 6760-6.

SCOP, 2009. Report of the Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants on the Work of Its Fourth Meeting; Stockholm Convention on Persistent Organic Pollutants: Geneva, 4-8 May 2009. http://chm.pops.int/Implementation/NewPOPs/TheNewPOPs/tabid/672/Default.aspx

Sellstrom, U., Bignert, A., Kierkegaard, A., Haggberg, L., De Wit, C.A., Olsson, M., Jansson, B., 2003. Temporal trend studies on tetra- and pentabrominated diphenyl ethers and hexabromocyclododecane in guillemot egg from the Baltic Sea. Environ. Sci. Technol. 37, 5496-501.

Shi, T., Chen, S.J., Luo ,X.J., Zhang, X.L., Tang, C.M., Luo, Y., Ma, Y.J., Wu, J.P., Peng, X.Z., Mai, B.X., 2009. Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China. Chemosphere 74, 910-6.

Shi, Z., Jiao, Y., Hu, Y., Sun, Z., Zhou, X., Feng, J., Li, J., Wu, Y., 2013. Levels of tetrabromobisphenol A, hexabromocyclododecanes and polybrominated diphenyl ethers in human milk from the general population in Beijing, China. Sci. Total Environ. 452-3, 10-8.

Sidorovich, V., 2000. Distribution and population density of the Otter (Lutra lutra) and pollution of aquatic ecosystems in Belarus. In: Conroy, J.W.H., Yoxon, P., Gutleb, A.C. (Eds.). Proceedings of the First Otter Toxicology Conference, vol. 1, Isle of Skye, 83-93.

Sjödin, A., Carlsson, H., Thuresson, K., Sjölin, S., Bergman, A., Ostman, C., 2001. Flame retardants in indoor air at an electronics recycling plant and at other work environments. Environ. Sci. Technol. 35, 448-54.

Sjödin, A., Hagmar, L., Klasson-Wehler, E., Kronholm-Diab, K., Jakobsson, E., Bergman, A., 1999. Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. Environ. Health. Perspect. 107, 643-8.

Sjödin, A., Jones, R.S., Focant, F.J., Lapeza, C., Wang, R.Y., McGahee, E.E., Zhang, Y., Turner, W.E., Slazyk, B., Needham, L.L., Patterson, D.G., 2004. Retrospective timetrend study of polybrominated diphenyl ethers and polybrominated and polychlorinated biphenyl levels in human serum from the United States. Environ. Health. Perspect. 112, 654-8.

Song, W.L., Ford, J.C., Li, A., Mills, W.J., Buckley, D.R., Rockne, K.J., 2004. Polybrominated

diphenyl ethers in the sediments of the Great Lakes. 1. Lake Superior. Environ. Sci. Technol. 38, 286-93.

Song, W.L., Ford, J.C., Li, A., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005a. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 3. Lakes Ontario and Erie. Environ. Sci. Technol. 39, 5600-5.

Song, W.L., Li, A., Ford, J.C., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005b. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 2. Lakes Michigan and Huron. Environ. Sci. Technol. 39, 3474-9.

Stapleton, H.M., Allen, J.G., Kelly, S.M., Konstantinov, A., Klosterhaus, S., Watkins, D., McClean, M.D., Webster, T.F., 2008. Alternate and new brominated flame retardants detected in US house dust. Environ. Sci. Technol. 42, 6910-6.

Stapleton, H.M., Dodder, N.G., Kucklick, J.R., Reddy, C.M., Schantz, M. M., Becker, P.R., Gulland, F., Porter, B.J., Wise, S.A., 2006. Determination of HBCD, PBDEs and MeO-BDEs in California sea lions (Zalophus californianus) stranded between 1993 and 2003. Mar. Pollut. Bull. 52, 522-31.

Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. Environ. Sci. Technol. 43, 7490-5.

Stewart, M., Olsen, G., Hickey, C.W., Ferreira, B., Jelić, A., Petrović, M., Barcelo, D., 2014. A survey of emerging contaminants in the estuarine receiving environment around Auckland, New Zealand. Sci. Total Environ. 468-9, 202-10.

Streets, S.S., Henderson, S.A., Stoner, A.D., Carlson, D.L., Simcik, M.F., Swackhamer, D.L., 2006. Partitioning and Bioaccumulation of PBDEs and PCBs in Lake Michigan. Environ. Sci. Technol. 40, 7263-9.

Sugiura, K., 1992. Microbial degradation of polychlorinated biphenyls in aquatic environments. Chemosphere 24, 881-90.

Sun, P., Basu, I., Blanchard, P., Brice, K.A., Hites, R.A., 2007. Temporal and spatial trends of atmospheric polychlorinated biphenyl concentrations near the Great Lakes. Environ. Sci. Technol. 41, 1131-6.

Sverko, E., Tomy, G.T., Marvin, C.H., Zaruk, D., Reiner, E., Helm, P.A., Hill, B., McCarry, B.E., 2008. Dechlorane plus levels in sediment of the lower Great Lakes. Environ. Sci. Technol. 42, 361-6.

Swackhamer, D.L., McVeety, B.D., Hites, R.A., 1988. Deposition and evaporation of polychlorobiphenyl congeners to and from Siskiwit Lake, Isle Royale, Lake Superior. Environ. Sci. Technol. 22, 664-72.

Tan, J., Cheng, S.M., Loganath, A., Chong, Y.S., Obbard, J.P., 2007. Selected organochlorine

pesticide and polychlorinated biphenyl residues in house dust in Singapore. Chemosphere 68, 1675-82.

Tapie, N., Le Menach, K., Pasquaud, S., Elie, P., Devier, M.H., Budzinski, H., 2011. PBDE and PCB contamination of eels from the Gironde estuary: from glass eels to silver eels. Chemosphere 83, 175-85.

Teil, M.J., Tlili, K., Blanchard, M., Labadie, P., Alliot, F., Chevreuil, M., 2014. Polychlorinated biphenyls, polybrominated diphenyl ethers, and phthalates in roach from the seine river basin (france): impact of densely urbanized areas. Arch. Environ. Contam. Toxicol. 66, 41-57.

Thomas, G.O., Wilkinson, M., Hodson, S., Jones, K.C., 2006. Organohalogen chemicals in human blood from the United Kingdom. Environ. Pollut. 141, 30-41.

Thomsen, C., Knutsen, H.K., Liane, V.H., Frøshaug, M., Kvalem, H.E., Haugen, M., Meltzer, H.M., Alexander, J., Becher, G., 2008. Consumption of fish from a contaminated lake strongly affects the concentrations of polybrominated diphenyl ethers and hexabromocyclododecane in serum. Mol. Nutr. Food Res. 52, 228-37.

Thomsen, C., Liane, V.H., Becher, G., 2007a. Automated solid-phase extraction for the determination of polybrominated diphenyl ethers and polychlorinated biphenyls in serum-application on archived Norwegian samples from 1977-2003. J. Chromatogr. B. Analyt. Technol. Biomed. Life. Sci. 846, 252-63.

Thomsen, C., Lundanes, E., Becher, G., 2002. Brominated flame retardants in archived serum samples from Norway: a study on temporal trends and the role of age. Environ. Sci. Technol. 36, 1414-8.

Thomsen, C., Molader, P., Daae, H.L., Janaak, K., Froshaug, M., Liane, V.H., Thorud, S., Becher, G., Dybing, E., 2007b. Occupational Exposure to Hexabromocyclododecane at an Industrial Plant. Environ. Sci. Technol. 41, 5210-6.

Tittlemier, S.A., Halldorson, T., Stern, G.A., Tomy, G.T., 2002. Vapor pressures, aqueous solubilities, and Henry's law constants of some brominated flame retardants. Environ. Toxicol. Chem. 21, 1804-10.

Toms, L.M., Mortimer, M., Symons, R.K., Paepke, O., Mueller, J.F., 2008. Polybrominated diphenyl ethers (PBDEs) in sediment by salinity and land-use type from Australia. Environ. Int. 34, 58-66.

Toms, L.M.L., Sjödin, A., Harden, F., Hobson, P., Jones, R., Edenfield, E., Mueller, J.F., 2009. Serum Polybrominated Diphenyl Ether (PBDE) Levels Are Higher in Children (2-5 Years of Age) than in Infants and Adults. Environ. Health. Perspect. 117, 1461-65.

Tomy, G.T., Palace, V.P., Pleskach, K., Ismail, N., Oswald, T., Danell, R., Wautier, K., Evans, B., 2007. Dietary exposure of juvenile rainbow trout (Oncorhynchus mykiss) to 1,2-bis(2,4,6-tribromo-phenoxy)ethane: bioaccumulation parameters, biochemical effects,

and metabolism. Environ. Sci. Technol. 41, 4913-8.

Tseng, L.H., Lee, C.W., Pan, M.H., Tsai, S.S., Li, M.H., Chen, J.R., Lay, J.J., Hsu, P.C., 2006. Postnatal exposure of the male mouse to 2,2′,3,3′,4,4′,5,5′,6,6′-decabrominated diphenyl ether: Decreased epididymal sperm functions without alterations in DNA content and histology in testis. Toxicology 224, 33-43.

UBA Umweltbundesamt. No. 40/2001 UBAFB Nr 000171/1e.

Ulbrich, B., Stahlmann, R., 2004. Developmental toxicity of polychlorinated biphenyls (PCBs): a systematic review of experimental data. Arch. Toxicol. 78, 252-68.

UNEP, Stockholm Convention on Persistent Organic Pollutants-HBCD risk management evaluation.
http://www.google.co.uk/url?sa=t&rct=j&q=&esrc=s&frm=1&source=web&cd=2&cad=rja&ved=0CDMQFjAB&url=http%3A%2F%2Fchm.pops.int%2FPortals%2F0%2Fdownload.aspx%3Fd%3DUNEP-POPS-POPRC.7-19-Add.1.English.pdf&ei=AMbrUt-pLIrF7AbvkIGYBw&usg=AFQjCNEBs2oa_bkTkjrrx4HUh_4NI1UG6g&sig2=BUndodQJklMuUzOZmTCOvg&bvm=bv.60444564,d.bGQ

USEPA (United States Environmental Protection Agency), 2002. National recommended water quality criteria: EPA-822-R-02-047. (http://www.epa.gov/ost/pc/revcom.pdf).

USEPA 1996. PCBs: a cancer dose–response assessment and applications to environmental mixtures. EPA/600/P-96/001F.

USEPA Inventory Update Reporting (http://www.epa.gov/oppt/cdr/index.html).

USEPA Inventory Update Rule 2002. Non-confidential production volume information submitted by companies for chemicals under the 1986-2002 inventory update rule (IUR).

USEPA. Environmental Protection Agency, Fed. Regist. 1985, 50, 46785.

USEPA. Environmental Protection Agency. Fed. Regist. 1988, 53, 47228.

USEPA. Technical Fact Sheet - Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Biphenyls (PBBs), May 2012.

van der Ven, L.T., Verhoef, A., van de Kuil, T., Slob, W., Leonards, P.E.G., Visser, T.J., Hamers, T., Herlin, M., Hakansson, H., Olausson, H., Piersma, A.H., Vos, J.G., 2006. A 28- day oral dose toxicity study enhanced to detect endocrine effects of hexabromocyclododecane in wistar rats. Toxicol. Sci. 94, 281-92.

Van Esch, G.J., 1997. Environmental health criteria 192- Flame Retardants: A General Introduction. World Health Organization.

Van Oostdam, J., Donaldson, S.G., Feeley, M., Arnold, D., Ayotte, P., Bondy, G., Chan, L., Dewaily, E., Furgal, C.M., Kuhnlein, H., Loring, E., Muckle, G., Myles, E., Receveur, O., Tracy, B., Gill, U., Kalhok, S., 2005. Human health implications of environmental contaminants in Arctic Canada: A review. Sci. Total Environ. 351-2:165-246.

Vane, C.H., Ma, Y.J., Chen, S.J., Mai, B.X., 2010. Increasing polybrominated diphenyl ether (PBDE) contamination in sediment cores from the inner Clyde Estuary, UK. Environ. Geochem. Health. 32, 13-21.

VECAP 2012. http://www.vecap.info/uploads/report2012.pdf

Vilanova, R., Fernández, P., Martínez, C., Grimalt, J.O., 2001. Organochlorine Pollutants in Remote Mountain Lake Waters. J. Environ. Aual. 30, 1286-95.

Voorspoels, S., Covaci, A., Schepens, P., 2004. PBDEs in sediments from a polluted area in Europe: The Belgian North Sea, the Western Scheldt Estuary and tributaries. In: Proceedings of the Third International Workshop on Brominated Flame Retardants BFR 2004, Toronto, Canada, 133-6.

Vorkamp, K., Bossi, R., Bester, K., Bollmann, U.E., Boutrup, S., 2014. New priority substances of the European Water Framework Directive: Biocides, pesticides and brominated flame retardants in the aquatic environment of Denmark. Sci. Total Environ. 470-1, 459-68.

Wan, X., Pan, X.J., Wang, B., Zhao, S.M., Hu, P., Li, F., Boulanger, B., 2011. Distributions, historical trends, and source investigation of polychlorinated biphenyls in Dianchi Lake, China. Chemosphere 85, 361-7.

Ward, E.M., Schulte, P., Grajewski, B., Andersen, A., Patterson, D.G.Jr., Turner, W., Jellum, E., Deddens, J.A., Friedland, J., Roeleveld, N., Waters, M., Butler, M.A., DiPietro, E., Needham, L.L., 2000. Serum organochlorine levels and breast cancer: a nested case-control study of Norwegian women. Cancer Epidemiol. Biomarkers Prev. 9, 1357-67.

Watanabe, I., Sakai, S. 2003. Environmental release and behavior of brominated flame retardants. Environ. Int. 29, 665-82.

Webster, L., Russell, M., Adefehinti, F., Dalgarno, E.J., Moffat, C.F., 2008. Preliminary assessment of polybrominated diphenyl ethers (PBDEs) in the Scottish aquatic environment, including the firth of Clyde. J. Environ. Monit. 10, 463-73.

Weiss, J., Meijer, L., Sauer, P., Linderholm, L., Bergman, A., Athanassiadis, I., 2004. PBDE and HBCD levels in blood from Dutch mothers and infants – analysis of a Dutch Groningen infant cohort. Organohalogen Compd. 66, 2677-82.

WFD, Directive 2013/39/EU. 2013. Official journal of the European Union. L226, 1-17.

WHO 1992. World Health Organization, Polychlorinated biphenyls and terphenyls, IPCS, Environmental health criteria 140, Geneva, Switzerland.

Wu, F.,Guo, J., Chang, H., Liao, H, Zhao, X., Mai, B., Xing, B., 2012. Polybrominated diphenyl ethers and decabromodiphenylethane in sediments from twelve lakes in China. Environ. Pollut. 162, 262-8.

Wu, J.P., Guan, Y.T., Zhang, Y., Luo, X.J., Zhi, H., Chen, S.J., Mai, B.X., 2010. Trophodynamics of hexabromocyclododecanes and several other non-PBDE brominated flame retardants in a

freshwater food web. Environ. Sci. Technol. 44, 5490-5.

Wu, J.P., Luo, X.J., Zhang, Y., Luo, Y., Chen, S.J., Mai, B.X., Yang, Z.Y., 2008. Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site in South China. Environ. Int. 34, 1109-13.

Wu, N., Herrmann, T., Paepke, O., Tickner, J., Hale, R., Harvey, L.E., La Guardia, M., McClean, M.D., Webster, T.F., 2007. Human exposure to PBDEs: associations of PBDE body burdens with food consumption and house dust concentrations. Environ. Sci. Technol. 41, 1584-9.

Xu, J., Zhang, Y., Guo, C., He, Y., Li, L., Meng, W., 2013. Levels and distribution of tetrabromobisphenol A and hexabromocyclododecane in Taihu Lake, China. Environ Toxicol Chem. 32, 2249-55.

Yan, S., Rodenburg, L.A., Dachs, J., Eisenreich, S.J., 2008. Seasonal air-water exchange fluxes of polychlorinated biphenyls in the Hudson River Estuary. Environ. Pollut. 152, 443-51.

Yang, R., Wei, H., Guo, J., Li, A., 2012. Emerging Brominated Flame Retardants in the Sediment of the Great Lakes. Environ. Sci. Technol. 46, 3119-3126.

Yu, J., Wang, T., Han, S., Wang, P., Zhang, Q., Jiang, G., 2013. Distribution of polychlorinated biphenyls in an urban riparian zone affected by wastewater treatment plant effluent and the transfer to terrestrial compartment by invertebrates. Sci. Total Environ. 463-4, 252-7.

Yuan, J., Chen, L., Chen, D., Guo, H., Bi, X., Ju, Y., Jiang, P., Shi, J., Yu, Z., Yang, J., Li, L., Jiang, Q., Sheng, G., Fu, J., Wu, T., Chen, X., 2008. Elevated serum polybrominated diphenyl ethers and thyroid-stimulating hormone associated with lymphocytic micronuclei in Chinese workers from an E-waste dismantling site. Environ. Sci. Technol. 42, 2195-200.

Zegers, B.N., Lewis, W.A., Booij, K., Smittenberg, R.H., Boer, W., de Boer, J., Boon, J.P., 2003. Levels of polybrominated diphenyl ether flame retardants in sediment cores from Western Europe. Environ. Sci. Technol. 37, 3803-7.

Zegers, B.N., Mets, A., vanBommel, R., Minkenberg, C., Hamers, T., Kamstra, J.H., Pierce, G.J., Boon, J.P., 2005. Levels of hexabromocyclododecane in harbor porpoises and common dolphins from Western European Seas, with evidence for stereoisomer-specific biotransformation by cytochrome P450. Environ. Sci. Technol. 39, 2095-100.

Zennegg, M., Kohler, M., Hartmann, P.C., Sturm, M., Gujer, E., Schmid, P., Gerecke, A.C., Heeb, N.V., Kohler, H.P., Giger, W., 2007. The historical record of PCB and PCDD/F deposition at Greifensee, a lake of the Swiss plateau, between 1848 and 1999. Chemosphere 67, 1754-61.

Zhang, S., Zhang, Q., Darisaw, S., Ehie, O., Wang, G., 2007. Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA. Chemosphere. 66, 1057-69.

Zhang, X., Diamond, M.L., Robson, M., Harrad, S., 2011a. Sources, emissions, and fate of polybrominated diphenyl ethers and polychlorinated biphenyls indoors in Toronto, Canada. Environ. Sci. Technol. 45, 3268-74.

Zhang, X., Yang, F., Luo, C., Wen, S., Zhang, X., Xu, Y., 2009a. Bioaccumulative characteristics of hexabromocyclododecanes in freshwater species from an electronic waste recycling area in China. Chemosphere. 76, 1572-8.

Zhang, X., Zhang D.D., Luo, Z.X., Lin, L.F., Yan., C.Z., 2011b. Diastereoisomer- and enantiomer-specific profiles of hexabromocyclododecane in the sediment of Dongjiang River, South China. Environ. Chem. 8, 561-8.

Zhang, X.L., Luo, X.J., Chen, S.J., Wu, J.P., Mai, B.X., 2009b. Spatial distribution and vertical profile of polybrominated diphenyl ethers, tetrabromobisphenol A, and decabromodiphenylethane in river sediment from an industrialized region of South China. Environ. Pollut. 157, 1917-23.

Zhang, Y., Sun, H., Liu, F., Dai, Y., Qin, X., Ruan, Y., Zhao, L., Gan, Z., 2013. Hexabromocyclododecanes in limnic and marine organisms and terrestrial plants from Tianjin, China: diastereomer- and enantiomer-specific profiles, biomagnification, and human exposure. Chemosphere. 93, 1561-8.

Zhang, Z., Huang, J., Yu, G., Hong, H., 2004. Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environ. Pollut. 130, 249-61.

Zhao, R.S., Hu, C., Zhou, J.B., Yuan, J.P., Wang, S.S., Wang, X., 2011a. Preconcentration and sensitive determination of hexabromocyclododecane diastereomers in environmental water samples using solid phase extraction with bamboo charcoal cartridge prior to rapid resolution liquid chromatography- electrospray tandem mass spectrometry. Anal. Bioanal. Chem. 400, 1189-95.

Zhao, X., Zhang, H., Ni, Y., Lu, X., Zhang, X., Su, F., Fan, J., Guan, D., Chen, J., 2011b. Polybrominated diphenyl ethers in sediments of the Daliao River Estuary, China: Levels, distribution and their influencing factors. Chemosphere 82, 1262-1267.

Zheng, J., Luo, X.J., Yuan, J.G., Wang, J., Wang, Y.T., Chen, S.J., Mai, B.X., Yang, Z.Y., 2011. Levels and sources of brominated flame retardants in human hair from urban, e-waste, and rural areas in South China. Environ. Pollut. 159, 3706-13.

Zhu, H., Wang, Y., Wang, X., Luan, T., Tam, N.F., 2014. Distribution and accumulation of polybrominated diphenyl ethers (PBDEs) in Hong Kong mangrove sediments. Sci. Total Environ. 468-9, 130-9.

Appendix A: Data Tables

Table 1 Part 1: Concentrations[a] of "legacy" and "novel" BFRs (ng g^{-1} TOC) in sediment core segments from HOLT

Concentrations									
Compound \ Average Year	2009	2003	1997	1991	1986	1981	1976	1971	1966
ΣPCBs[b]	32.4	63.4	95.1	195	160	135	144	156	11.8
ΣHBCDs[c]	9.66	11.0	29.5	23.4	16.3	12.7	9.68	0.76	0.90
Σtri-hexa-BDEs[d]	5.86	5.07	5.17	3.78	2.47	1.51	1.06	0.64	<0.01
BDE 183	0.59	1.40	0.51	0.57	0.51	0.23	<0.12	<0.12	<0.12
BDE 209	26.7	19.4	9.45	13.6	7.97	5.64	2.52	3.53	3.35
TBPH	183	130	86.0	47.7	64.0	8.52	<0.84	<0.84	<0.84
PBEB	7.63	8.34	10.3	3.87	2.11	1.33	0.83	<0.02	<0.02
EHTBB	2.42	1.19	1.45	0.90	0.25	0.59	<0.03	<0.03	<0.03
TBBPA-DBPE	4.96	2.29	2.56	3.06	2.39	2.29	1.10	<0.79	<0.79
BTBPE	0.74	0.75	0.83	0.53	0.39	0.37	<0.01	<0.01	<0.01
DBDPE	2.44	1.09	0.46	0.28	0.18	<0.18	<0.18	<0.18	<0.18
HCDBCO	12.7	7.56	13.4	6.69	10.3	7.06	4.29	2.65	3.90
TBECH	0.49	0.27	0.33	0.33	0.40	0.37	0.18	0.25	<0.03
HBB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBCC	4.04	1.69	2.35	1.77	1.19	0.87	0.34	<0.01	<0.01
PBBB	1.88	0.60	0.68	0.12	<0.11	<0.11	<0.11	<0.11	<0.11
sDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
aDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ΣDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Limit of quantification (LOQ, ng g^{-1} TOC) was reported where compound was found below detection limits

[b] sum of PCB-28, -52, -101, -118, -153, -138, -180; [c] sum of α-, β-, and γ-HBCD isomers; [d] sum of BDE-17, -28, -49, -47, -66, -100, -99, -99, -85, -154, and -153

Table 1 Part 2: Concentrations[a] of "legacy" and "novel" BFRs (ng g^{-1} TOC) in sediment core segments from MARM

Concentrations											
Compound \ Average Year	2009	2003	1997	1993	1988	1982	1977	1971	1964	1958	1952
ΣPCBs[b]	73.5	125	176	228	228	371	478	514	317	285	144
ΣHBCDs[c]	6.76	5.87	5.27	4.80	6.01	14.3	10.7	4.40	1.09	<0.005	<0.005
Σtri-hexa-BDEs[d]	8.89	6.41	3.78	1.68	1.20	1.05	0.32	<0.01	<0.01	<0.01	<0.01
BDE 183	1.91	4.80	3.69	4.09	3.24	0.74	<0.12	<0.12	<0.12	<0.12	<0.12
BDE 209	183	156	106	87.8	107	17.8	14.2	3.49	3.43	3.58	1.91
TBPH	244	188	139	71.9	60.5	47.8	18.2	<0.84	<0.84	<0.84	<0.84
PBEB	11.2	17.0	24.0	18.4	23.1	5.71	1.07	<0.02	<0.02	<0.02	<0.02
EHTBB	2.00	1.67	1.91	1.41	1.32	1.18	0.42	<0.03	<0.03	<0.03	<0.03
TBBPA-DBPE	31.7	18.7	11.2	16.8	15.0	8.93	1.83	<0.79	<0.79	<0.79	<0.79
BTBPE	0.94	1.00	1.05	0.67	1.08	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBDPE	2.19	1.52	0.74	0.38	0.69	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
HCDBCO	3.57	10.6	7.77	8.05	11.2	17.0	4.79	<0.03	<0.03	<0.03	<0.03
TBECH	2.33	2.03	1.12	1.64	1.62	0.32	<0.03	<0.03	<0.03	<0.03	<0.03
HBB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBCC	0.85	0.77	0.50	0.60	0.37	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBBB	6.37	4.34	2.47	1.64	1.38	0.48	<0.11	<0.11	<0.11	<0.11	<0.11
sDP	0.41	0.40	0.47	0.53	0.68	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
aDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ΣDP	0.41	0.40	0.47	0.53	0.68	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Limit of quantification (LOQ, ng g^{-1} TOC) was reported where compound was found below detection limits

[b] sum of PCB-28, -52, -101, -118, -153, -138, -180; [c] sum of α-, β-, and γ-HBCD isomers; [d] sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153

Table 1 Part 3: Concentrations[a] of "legacy" and "novel" BFRs (ng g^{-1} TOC) in sediment core segments from PFLE

Concentration											
Average Year / Compound	2009	2003	1997	1991	1985	1980	1976	1971	1966	1960	1954
ΣPCBs[b]	74.0	74.5	77.2	74.3	79.8	85.8	95.2	86.4	96.9	53.8	44.5
ΣHBCDs[c]	13.4	10.5	12.0	22.4	23.3	15.3	17.4	10.7	17.2	7.78	0.50
Σtri-hexa-BDEs[d]	6.00	8.42	9.04	5.70	6.42	6.01	5.44	2.43	3.49	0.08	<0.01
BDE 183	1.02	1.05	0.93	0.64	1.07	0.71	0.59	0.98	0.56	<0.12	<0.12
BDE 209	115	91.4	104	88.9	81.6	59.6	73.6	61.8	47.7	17.2	8.43
TBPH	412	283	267	167	129	209	24.7	16.4	<0.84	<0.84	<0.84
PBEB	21.8	15.9	22.4	18.3	17.2	20.2	14.7	18.9	15.7	12.7	<0.02
EHTBB	3.17	2.96	4.44	3.30	1.74	1.72	2.11	2.73	1.03	0.86	<0.03
TBBPA-DBPE	51.8	32.7	67.7	29.9	10.7	20.1	6.95	8.82	<0.79	<0.79	<0.79
BTBPE	2.96	1.46	1.01	0.73	0.51	0.35	<0.01	<0.01	<0.01	<0.01	<0.01
DBDPE	4.79	2.88	2.61	1.47	1.50	0.90	<0.18	<0.18	<0.18	<0.18	<0.18
HCDBCO	29.8	30.2	31.6	26.1	18.5	34.2	38.3	36.0	44.5	<0.03	<0.03
TBECH	0.69	0.40	1.22	0.59	0.82	0.61	0.36	0.35	0.48	<0.03	<0.03
HBB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBCC	0.35	0.32	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBBB	3.33	3.84	4.32	3.87	4.19	4.56	4.94	2.66	3.43	<0.11	<0.11
sDP	0.77	0.44	0.22	0.33	0.28	0.35	<0.01	<0.01	<0.01	<0.01	<0.01
aDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ΣDP	0.77	0.44	0.22	0.33	0.28	0.35	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Limit of quantification (LOQ, ng g^{-1} TOC) was reported where compound was found below detection limits

[b] sum of PCB-28, -52, -101, -118, -153, -138, -180; [c] sum of α-, β-, and γ-HBCD isomers; [d] sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153

Table 1 Part 4: Concentrations[a] of "legacy" and "novel" BFRs (ng g^{-1} TOC) in sediment core segments from SLT

Concentration												
Compound \ Average Year	2009	2003	1998	1993	1987	1982	1977	1972	1966	1960	1956	1951
ΣPCBs[b]	10.8	15.2	18.5	22.1	26.4	35.6	28.2	30.9	29.2	27.2	35.7	19.9
ΣHBCDs[c]	1.22	19.8	3.93	0.97	0.68	1.15	0.25	0.23	0.32	0.22	0.14	0.13
Σtri-hexa-BDEs[d]	0.47	0.42	0.40	0.31	0.29	0.24	0.13	0.09	<0.01	<0.01	<0.01	<0.01
BDE 183	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
BDE 209	13.5	8.73	10.2	10.57	3.11	2.69	2.69	1.32	1.56	0.57	1.55	1.02
TBPH	38.9	33.8	67.0	24.3	13.8	10.6	8.90	4.98	<0.84	<0.84	<0.84	<0.84
PBEB	1.23	1.62	1.37	1.13	1.20	1.41	1.36	1.48	1.68	1.95	1.08	1.42
EHTBB	0.90	0.81	1.23	1.20	0.94	1.02	0.88	1.27	0.95	<0.02	<0.02	<0.02
TBBPA-DBPE	5.66	5.55	5.90	7.62	2.74	4.94	2.94	2.41	1.02	<0.79	<0.79	<0.79
BTBPE	0.12	0.03	0.07	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBDPE	0.82	0.45	0.70	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
HCDBCO	0.34	0.38	0.22	0.58	0.52	0.58	0.44	0.53	0.68	<0.03	<0.03	<0.03
TBECH	0.20	0.34	0.42	0.28	0.43	0.29	0.21	0.22	0.27	<0.03	<0.03	<0.03
HBB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBCC	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBBB	0.32	0.45	0.34	0.24	0.28	0.18	0.12	0.11	<0.11	<0.11	<0.11	<0.11
sDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
aDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ΣDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Limit of quantification (LOQ, ng g^{-1} TOC) was reported where compound was found below detection limits

[b] sum of PCB-28, -52, -101, -118, -153, -138, -180; [c] sum of α-, β-, and γ-HBCD isomers; [d] sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153

Table 1 Part 5: Concentrations[a] of "legacy" and "novel" BFRs (ng g^{-1} TOC) in sediment core segments from WAKE

Concentration											
Average Year / Compound	2009	2003	1998	1992	1986	1981	1976	1971	1966	1960	1956
ΣPCBs[b]	49.9	60.0	67.8	76.2	79.1	84.3	82.8	141	200	121	9.53
ΣHBCDs[c]	4.17	5.87	4.37	4.56	9.02	4.52	3.35	1.99	0.46	0.83	0.32
Σtri-hexa-BDEs[d]	2.43	1.36	2.55	1.69	1.34	0.98	0.75	1.07	<0.01	<0.01	<0.01
BDE 183	0.63	0.58	0.53	0.50	0.44	0.31	0.33	0.36	<0.12	<0.12	<0.12
BDE 209	32.9	17.9	27.0	15.6	19.4	21.7	17.3	6.10	2.54	0.68	<0.13
TBPH	167	118	59.9	45.2	52.4	54.6	42.0	<0.84	<0.84	<0.84	<0.84
PBEB	3.88	4.62	5.50	6.02	25.9	7.10	7.88	3.18	4.07	1.29	<0.02
EHTBB	1.51	1.23	1.63	1.11	1.43	1.10	1.55	0.71	0.69	<0.03	<0.03
TBBPA-DBPE	11.3	10.3	13.4	7.56	3.79	6.39	2.79	<0.79	<0.79	<0.79	<0.79
BTBPE	1.08	0.66	0.59	0.45	0.71	0.15	<0.01	<0.01	<0.01	<0.01	<0.01
DBDPE	2.01	0.99	1.04	0.73	0.65	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
HCDBCO	7.77	10.8	10.6	10.6	11.2	13.1	16.7	<0.03	<0.03	<0.03	<0.03
TBECH	0.43	0.54	0.77	0.80	1.07	0.49	1.25	<0.03	<0.03	<0.03	<0.03
HBB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBCC	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PBBB	1.89	1.69	2.00	1.65	1.87	1.41	0.98	0.11	<0.11	<0.11	<0.11
sDP	0.41	0.09	0.25	0.07	0.07	0.21	0.25	0.17	0.11	<0.01	<0.01
aDP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ΣDP	0.41	0.09	0.25	0.07	0.07	0.21	0.25	0.17	0.11	<0.01	<0.01

[a] Limit of quantification (LOQ, ng g^{-1} TOC) was reported where compound was found below detection limits

[b] sum of PCB-28, -52, -101, -118, -153, -138, -180; [c] sum of α-, β-, and γ-HBCD isomers; [d] sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153

Appendix B: Figures

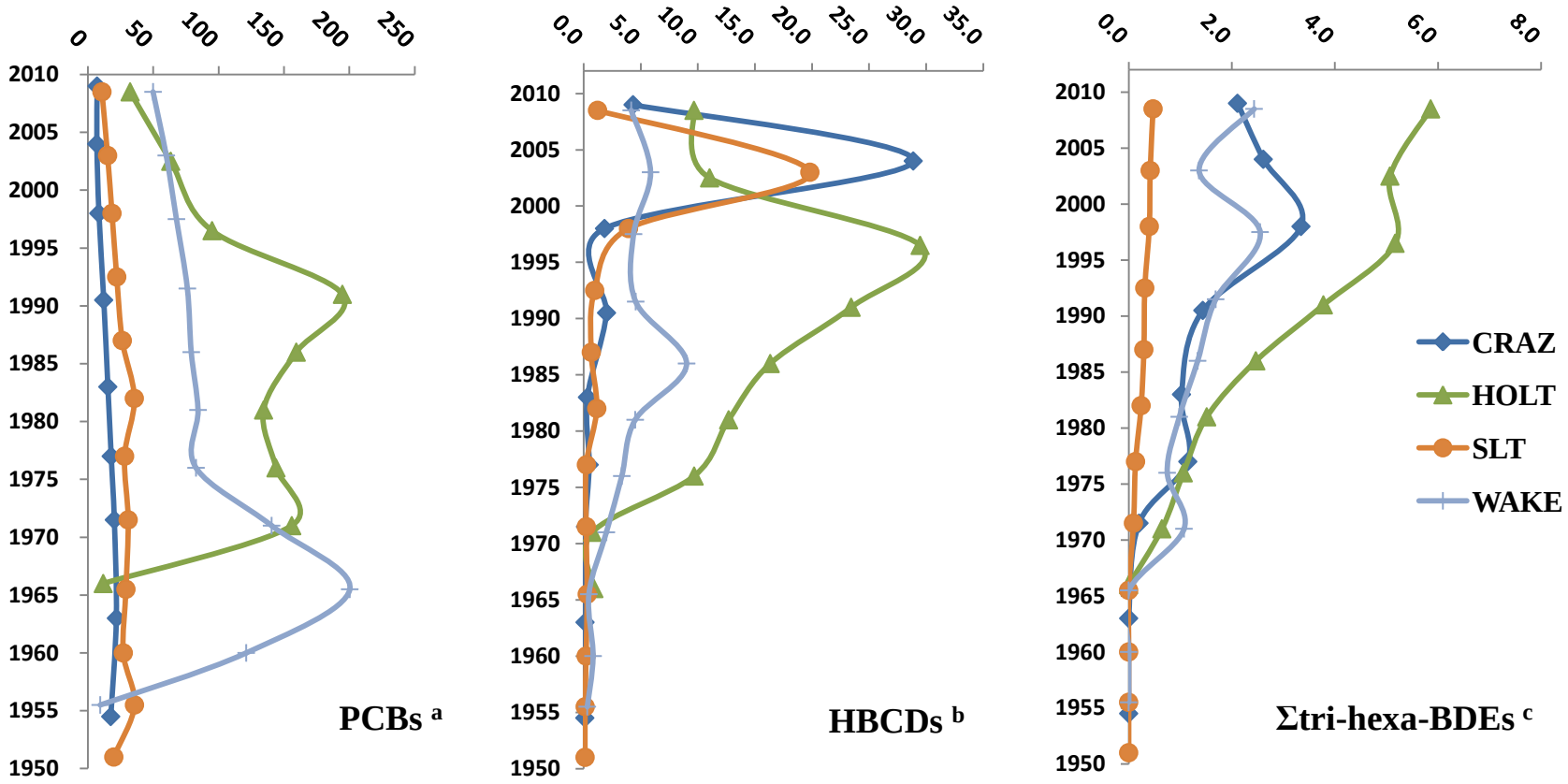


Figure 1 Part 1: Temporal trends of concentrations (ng g^{-1} TOC; x axis) of PCBs, HBCDs, and Σtri-hexa-BDEs in sediments from the CRAZ, HOLT, SLT, and WAKE, ~1950-2011/2; average year of sedimentation for each core slice plotted as the date

[a] sum of PCB-28, -52, -101, -118, -153, -138, -180; [b] sum of α-, β-, and γ-HBCD isomers; [c] sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153.

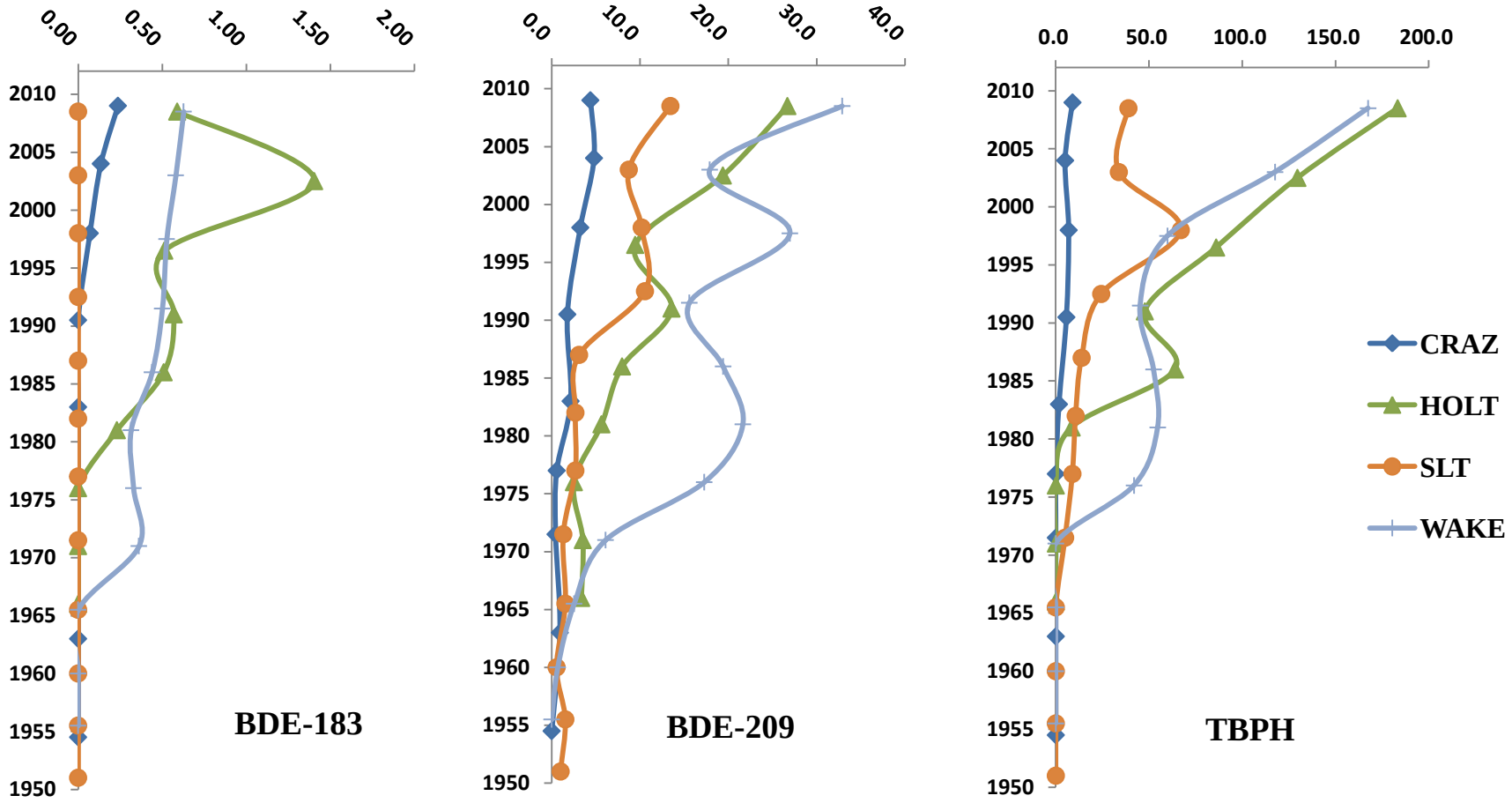


Figure 1 Part 2: Temporal trends of concentrations (ng g^{-1} TOC; x axis) of BDE-183, BDE-209, and TBPH in sediments from the CRAZ, HOLT, SLT, and WAKE, ~1950-2011/2; average year of sedimentation for each core slice plotted as the date

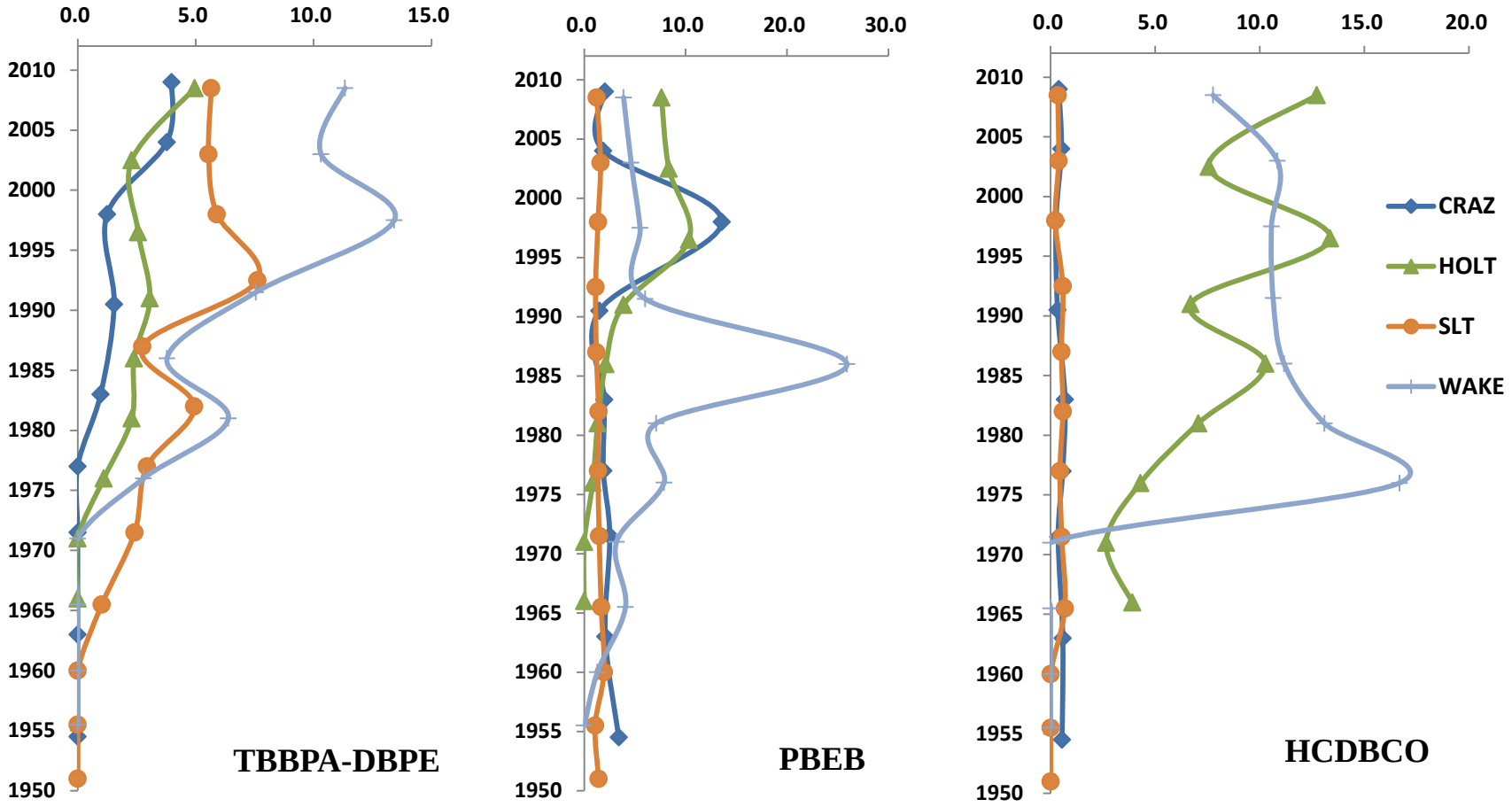


Figure 1 Part 3: Temporal trends of concentrations (ng g^{-1} TOC; x axis) of TBBPA-DBPE, PBEB, and HCDBCO in sediments from the CRAZ, HOLT, SLT, and WAKE, ~1950-2011/2; average year of sedimentation for each core slice plotted as the date

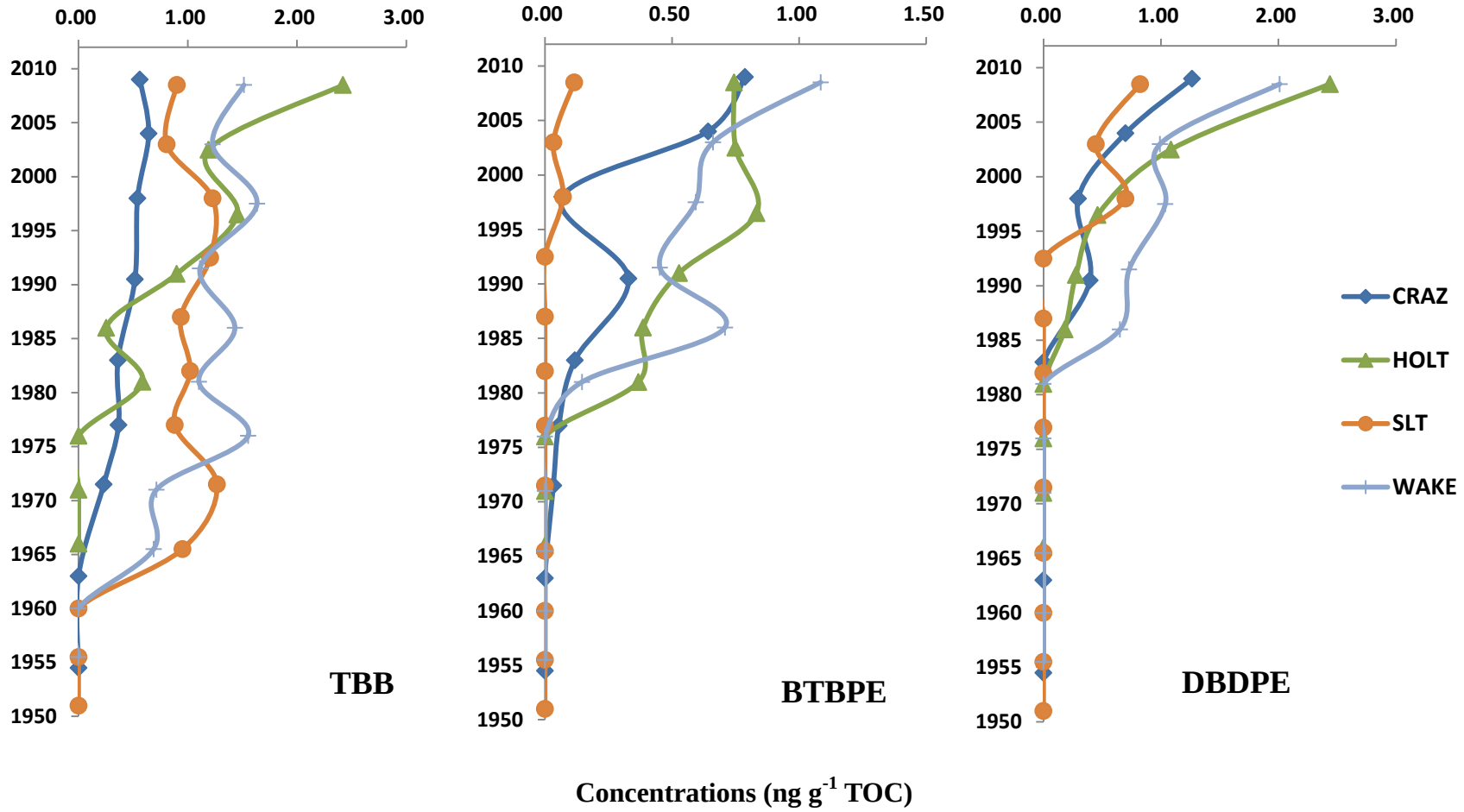


Figure 1 Part 4: Temporal trends of concentrations (ng g^{-1} TOC; x axis) of TBB, BTBPE, and DBDPE in sediments from the CRAZ, HOLT, SLT, and WAKE, ~1950-2011/2; average year of sedimentation for each core slice plotted as the date

Appendix C: List of Publications

1) Yang, C., Harrad, S., Abdallah, M., Desborough, J., Rose, N.L., Turner, S.D., Davidson, T.A., Goldsmith, B., 2014. Polybrominated diphenyl ethers (PBDEs) in English freshwater lakes, 2008-2012. Chemosphere 110, 41-7.

2) Jin, J., Wang, Y., Yang, C., Hu, J., Liu, W., Cui, J., Tang, X., 2009. Polybrominated diphenyl ethers in the serum and breast milk of the resident population from production area, China. Environ. Int. 35, 1048-52.

3) Jin, J., Yang, C., Wang, Y., Liu, A., 2009. Determination of Hexabromocyclododecane Diastereomers in Soil by Ultra Performance Liquid Chromatography-Electrospray Ion Source /Tandem Mass Spectrometry. Chin J. Anal. Chem. 37, 585-8.

   http://www.sciencedirect.com/science/article/pii/S1872204008600973

4) Jin, J., Wang, Y., Liu, W., Yang, C., Hu, J., Cui, J., 2011. Polybrominated diphenyl ethers in atmosphere and soil of a production area in China: Levels and partitioning. J. Environ. Sci. 23, 427-33.

5) Jin, J., Wang; Y., Yang, C., Hu, J., Liu, W., Cui, J., 2010. Human exposure to polybrominated diphenyl ethers at production area, China. Environ. Toxicol. Chem. 29, 1031-5.

6) Jin, J., Yang, C., Hu, J., Wang, Y., 2009. Hexabromocyclododecane in tree bark from Beijing, China. Organohalogen Compounds 71, 416-9.

7) Hu, J., Jin, J., Yang, C., Wang, Y., 2009. Levels of Polybrominated Diphenyl Ethers in tree bark from Beijing, China. Organohalogen Compounds 71, 430-3.

8) Yang, C., Jin, J., Wang, Y., Liu, W., 2008. The Environmental Level and Toxic effect of HBCD. Chinese J. Environ. Sci. Technol. 31, 174-8. (***in Chinese***)

9) Jin, J., Hu, J., Wang, Y., Yang, C., 2009. Atmospheric PBDEs in Spring Season, in Beijing, China. Chinese J. Environ. Chem. 28, 711-5. (***in Chinese***)